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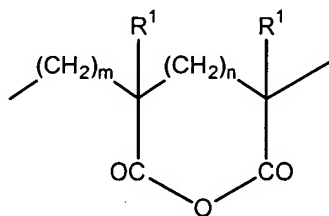
[Name of Document] SPECIFICATION

[Title of the Invention] ACRYLIC BLOCK COPOLYMER AND
THERMOPLASTIC RESIN COMPOSITION

[Claims]

[Claim 1] An acrylic block copolymer comprising a methacrylic polymer block (A) and an acrylic polymer block (B), at least one of the polymer blocks containing, in its main chain, at least one acid anhydride group (C) represented by formula (1):

[Chem. 1]



(wherein R¹s each represent a hydrogen atom or a methyl group and may be the same or different, n represents an integer of 0 to 3, and m represents an integer of 0 or 1).

[Claim 2] The acrylic block copolymer according to claim 1, containing 0.1% by weight to 50% by weight of a carboxyl group (D).

[Claim 3] The acrylic block copolymer according to claim 1 or 2, wherein the acrylic block copolymer is at least one selected from the group consisting of acrylic block copolymers represented by formulae (A-B)_n, B-(A-B)_n, and (A-

B)_n-A.

[Claim 4] The acrylic block copolymer according to claim 1, 2, or 3, wherein the number-average molecular weight is 30,000 to 500,000.

[Claim 5] The acrylic block copolymer according to claim 1, 2, 3, or 4, wherein the ratio (Mw/Mn) of the weight-average molecular weight (Mw) to the number-average molecular weight (Mn) according to gel permeation chromatographic measurement is 1 to 1.8.

[Claim 6] The acrylic block copolymer according to claim 1, 2, 3, 4, or 5, comprising 10% by weight to 60% by weight of the methacrylic polymer block (A) and 90% by weight to 40% by weight of the acrylic polymer block (B).

[Claim 7] The acrylic block copolymer according to claim 1, 2, 3, 4, 5, or 6, wherein the methacrylic polymer block (A) contains the acid anhydride group (C).

[Claim 8] The acrylic block copolymer according to claim 1, 2, 3, 4, 5, or 6, wherein the acrylic polymer block (B) contains the acid anhydride group (C).

[Claim 9] The acrylic block copolymer according to claim 7 or 8, wherein the content of the acid anhydride group (C) is 0.1% by weight to 99.9% by weight.

[Claim 10] The acrylic block copolymer according to claim 1, 2, 3, 4, 5, 6, 7, 8, or 9, wherein the carboxyl group (D) is contained in the block containing the acid anhydride

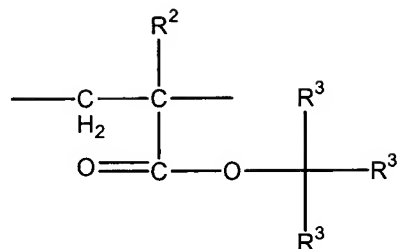
group (C).

[Claim 11] A thermoplastic resin composition comprising 0.5% by weight to 90% by weight of the acrylic block copolymer according to claim 1, 2, 3, 4, 5, 6, 7, 8, 9, or 10, and 99.5% by weight to 10% by weight of a thermoplastic resin (b) and/or a thermoplastic elastomer (c).

[Claim 12] The thermoplastic resin composition according to claim 11, wherein the thermoplastic resin (b) is selected from the group consisting of a polyvinyl chloride resin, a polymethyl methacrylate resin, an acrylonitrile-styrene copolymer resin, a methyl methacrylate-styrene copolymer resin, a polycarbonate resin, a polyester resin, and a polyamide resin, and the thermoplastic elastomer (c) is selected from the group consisting of a styrene elastomer, an olefin elastomer, a urethane elastomer, a vinyl chloride elastomer, an amide elastomer, an ester elastomer, and an acryl elastomer.

[Claim 13] A process for producing the acrylic block copolymer according to claim 1, 2, 3, 4, 5, 6, 7, 8, 9, or 10, the process comprising melt-kneading an acrylic block copolymer (d) at a temperature of 180°C to 300°C, the acrylic block copolymer (d) comprising a methacrylic polymer block (A) and an acrylic polymer block (B) at least one of which contains, in its main chain, at least one unit represented by formula (2):

[Chem. 2]



(wherein R² represents a hydrogen atom or a methyl group, and R³s each represent hydrogen, a methyl group, or a phenyl group, and may be the same or different as long as at least one R³ is a methyl group).

[Claim 14] The process according to claim 13, wherein the acrylic block copolymer (d) is produced by controlled radical polymerization.

[Claim 15] An acrylic block copolymer produced by hydrolyzing the acrylic block copolymer according to claim 1, 2, 3, 4, 5, 6, 7, 8, 9, or 10 to decyclize the acid anhydride group, wherein a carboxyl group (E) is present at a side chain.

[Claim 16] A process for producing the acrylic block copolymer according to claim 14, comprising melt-kneading the acrylic block copolymer according to claim 1, 2, 3, 4, 5, 6, 7, 8, 9, or 10 with water.

[Claim 17] An automobile, electric, or electronic part comprising the acrylic block copolymer according to claim 1, 2, 3, 4, 5, 6, 7, 8, 9, or 10, the acrylic block copolymer

according to claim 15, or the thermoplastic resin composition according to claim 11 or 12.

[Detailed Description of the Invention]

[0001]

[Technical Field of the Invention]

The present invention relates to nonconventional acrylic block copolymers and thermoplastic compositions which are rich in flexibility and excellent in mechanical strength, moldability, oil resistance, heat resistance, thermal decomposition resistance and is further rich in reactivity. The present invention also relates to automobile, electric, and electronic parts all of which are produced using the acrylic block copolymers or thermoplastic compositions.

[0002]

[Description of the Related Art]

Although vulcanized rubber has excellent flexibility and excellent rubber elasticity, rubber must be mixed with an additive and vulcanized in molding to increase the molding cycle time and complicate the molding process, thereby causing a problem of moldability. Also, vulcanized rubber is disadvantageous in that it is not melted even by reheating after molding and vulcanization, and thus it cannot be post-processed by bonding or the like and is difficult to recycle after use.

[0003]

From this viewpoint, in recent years, thermoplastic elastomers have been increasingly used in place of vulcanized rubber. For example, in automobile vehicles, various seal parts such as glass run channels, weatherstrips, various boots, draining moldings, and the like are used. These parts are mostly made of vulcanized rubber, but lightweight and recyclable olefinic thermoplastic elastomers have been recently brought into use for some of the seal parts from the viewpoint of improvement in fuel consumption and environmental problems.

[0004]

A thermoplastic elastomer generally has an alloy structure including a rubber component (soft segment) exhibiting entropy elasticity, and a restrictive component (hard segment) which flows at high temperatures but inhibits plastic deformation at room temperature to give a reinforcing effect to the rubber component. For example, in a styrenic elastomer, a styrene block aggregates and functions as a hard segment, and a butadiene block or an isoprene block forms a matrix and functions as a soft segment. An olefinic elastomer has an alloy structure in which rubber such as EPDM or the like is dispersed in a PP resin or the like. Any type of thermoplastic elastomer can be thermoplastically processed by injection molding or the

like because the hard segment flows at high temperatures. However, conventional styrenic or olefinic thermoplastic elastomers are disadvantageous in that they have insufficient rubber elasticity and heat resistance (corresponding to compression set characteristics at high temperatures) in comparison to vulcanized rubber, and also have low oil resistance. On the other hand, as thermoplastic elastomers having excellent oil resistance, acrylic block copolymers having methacrylic blocks and acrylic blocks have been recently disclosed, as disclosed in Japanese Patent No. 2,553,134. Like the styrenic elastomers, these elastomers have excellent moldability, but have the disadvantage that they have low heat resistance. Also, the hard segments of thermoplastic elastomers flow at high temperatures, and thus the thermoplastic elastomers can be thermoplastically processed. However, when the thermal decomposition temperatures of the thermoplastic elastomers are lower than injection molding temperatures, the thermoplastic elastomers thermally deteriorate in some cases. In particular, methacrylic polymers are often decomposed to monomers at 170°C to 250°C by depolymerization (Polymer Handbook Third Edition: Wiley-Interscience 1989). When high-temperature heat stability is required, therefore, these polymers cannot be used disadvantageously.

[0005]

In addition, it has been known that thermoplastic elastomers are added for modifying resins, for example, improving the impact resistance of thermoplastic resins, or used as soft materials compounded with thermoplastic resins (refer to, for example, Japanese Unexamined Patent Application Publication No. 10-279738). The styrenic elastomers and olefinic elastomers can be used for modifying other nonpolar resins due to the polarity thereof. However, the elastomers are poor in compatibility with polar resins, and thus compatibilizers must be added for modifying polar resins, or compounds such as maleic anhydride or the like must be grafted to thermoplastic elastomers, for modifying the polar resins (refer to, for example, Japanese Unexamined Patent Application Publication Nos. 7-173390 and 2000-265033). In this case, modification can be achieved, but oil resistance deteriorates due to the characteristics of the styrenic or olefinic thermoplastic elastomers. Although the above-described acrylic block copolymers have higher oil resistance and compatibility than those of the styrenic or olefinic thermoplastic elastomers, modification is still insufficient. There is thus demand for development of thermoplastic elastomers excellent in oil resistance, heat resistance, and thermal decomposition resistance, and also excellent for modification of thermoplastic resins and excellent in compounding characteristics.

[0006]

[Problems to be Solved by the Invention]

The present invention relates to a novel acrylic block copolymer rich in flexibility and excellent in mechanical strength, moldability, oil resistance, heat resistance, and thermal decomposition resistance, and also rich in reactivity, and also relates to compositions and automobile, electric, and electronic parts, each of which includes the acrylic block copolymer.

[0007]

[Means for Solving the Problems]

As a result of studies for solving the above-described problems, it was found that an acrylic block copolymer including a methacrylic polymer block (A) and an acrylic polymer block (B), at least one of the polymer blocks containing a specified acid anhydride group in its main chain, is rich in flexibility and excellent in mechanical strength, moldability, oil resistance, heat resistance, and thermal decomposition resistance, and is further rich in reactivity. This finding resulted in the completion of the present invention.

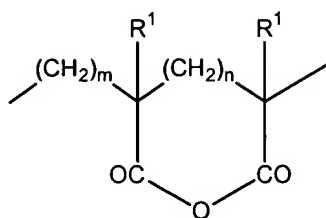
[0008]

Namely, the present invention relates to an acrylic block copolymer (a) including a methacrylic polymer block (A) and an acrylic polymer block (B) at least one of which

contains, in its main chain, at least one acid anhydride group (C) represented by formula (1):

[0009]

[Chem. 3]



[0010]

(wherein R^1 's each represent a hydrogen atom or a methyl group and may be the same or different, n represents an integer of 0 to 3, and m represents an integer of 0 or 1).

[0011]

The acrylic block copolymer (a) preferably contains 0.1% by weight to 50% by weight of a carboxyl group (D).

[0012]

The acrylic block copolymer is preferably at least one selected from the group consisting of acrylic block copolymers represented by formulae $(A-B)_n$, $B-(A-B)_n$, and $(A-B)_n-A$.

[0013]

The acrylic block copolymer preferably has a number-average molecular weight of 30,000 to 500,000 and a ratio (M_w/M_n) of 1 to 1.8 of the weight-average molecular weight

(Mw) to the number-average molecular weight (Mn) according to gel permeation chromatographic measurement.

[0014]

The acrylic block copolymer (a) preferably comprises 10% by weight to 60% by weight of the methacrylic polymer block (A) and 90% by weight to 40% by weight of the acrylic polymer block (B). The methacrylic polymer block (A) or the acrylic polymer block (B) may contain the acid anhydride group (C).

[0015]

The content of the acid anhydride group (C) is preferably 0.1% by weight to 99.9% by weight, and the carboxyl group (D) is preferably contained in the block containing the acid anhydride group (C).

[0016]

The present invention also relates to a thermoplastic resin composition comprising 0.5% by weight to 90% by weight of the acrylic block copolymer (a), and 99.5% by weight to 10% by weight of a thermoplastic resin (b) and a thermoplastic elastomer (c).

[0017]

The thermoplastic resin (b) is preferably selected from the group consisting of a polyvinyl chloride resin, a polymethyl methacrylate resin, an acrylonitrile-styrene copolymer resin, a methyl methacrylate-styrene copolymer

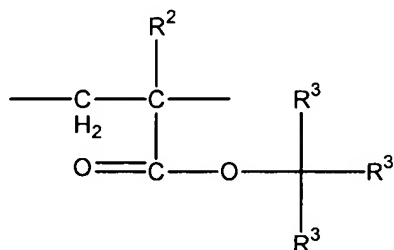
resin, a polycarbonate resin, a polyester resin, and a polyamide resin. The thermoplastic elastomer (c) is preferably selected from the group consisting of a styrene elastomer, an olefin elastomer, a urethane elastomer, a vinyl chloride elastomer, an amide elastomer, an ester elastomer, and an acryl elastomer.

[0018]

The present invention further relates to a process for producing the acrylic block copolymer (a) comprising melt-kneading an acrylic block copolymer (d) at a temperature of 180°C to 300°C, the acrylic block copolymer (d) comprising a methacrylic polymer block (A) and an acrylic polymer block (B) at least one of which contains, in its main chain, at least one unit represented by formula (2):

[0019]

[Chem. 4]



[0020]

(wherein R² represents a hydrogen atom or a methyl group, and R³s each represent a hydrogen atom, a methyl group, or a phenyl group, and may be the same or different as long as at least one R³ is a methyl group).

[0021]

The acrylic block copolymer (d) is preferably produced by controlled radical polymerization.

[0022]

The present invention further relates to an acrylic block copolymer (e) produced by hydrolyzing the acrylic block copolymer (a) to decyclize an acid anhydride group, wherein a carboxyl group (E) is present at a side chain.

[0023]

The acrylic block copolymer (e) is preferably produced by melt-kneading the acrylic block copolymer (a) with water. The present invention further relates to an automobile, electric, or electronic part comprising the acrylic block copolymer (a) or (e) or the thermoplastic resin composition.

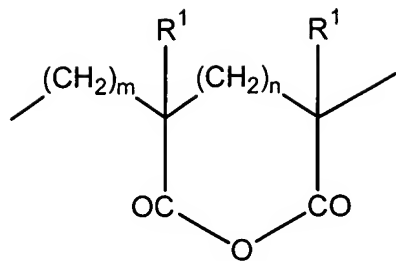
[0024]

[Description of the Embodiments]

The present invention relates to an acrylic block copolymer comprising a methacrylic polymer block (A) and an acrylic polymer block (B) at least one of which contains, in its main chain, at least one acid anhydride group (C) represented by formula (1):

[0025]

[Chem. 5]



[0026]

(wherein R¹s each represent a hydrogen atom or a methyl group and may be the same or different, n represents an integer of 0 to 3, and m represents an integer of 0 or 1). The present invention will be described in detail below.

[0027]

<Acrylic block copolymer (a)>

The acrylic block copolymer (a) of the present invention may have the structure of a linear block copolymer or a branched (star) block copolymer, or a mixture thereof. The structures of the block copolymer are properly used according to the required physical properties of the acrylic block copolymer (a) and the required processing properties and mechanical properties of a composition with a thermoplastic resin.

[0028]

The acrylic block copolymer (a) of the present invention may have the structure of a linear block copolymer or a branched (star) block copolymer, or a mixture thereof. The structures of the block copolymer are properly used

according to the required physical properties of the acrylic block copolymer (a) and the required processing properties and mechanical properties of a composition with a thermoplastic resin. However, in view of cost and polymerizability, a linear block copolymer is preferred.

[0029]

From the viewpoint of the physical properties of a composition, the linear acrylic block copolymer is preferably at least one selected from the group consisting of acrylic block copolymers represented by formulae $(A-B)_n$, $B-(A-B)_n$, and $(A-B)_n-A$ (n is an integer of 1 or more) wherein the methacrylic polymer block is denoted by A, and the acrylic polymer block is denoted by B. Although the type is not particularly limited, an (A-B)-diblock copolymer, an (A-B-A)-triblock copolymer, or a mixture thereof is particularly preferred from the viewpoint of handleability in processing and the physical properties of compositions.

[0030]

The number of the acid anhydride group (C) may be at least one per polymer block. When two or more acid anhydride groups are present, polymerization of a monomer containing the acid anhydride group is random copolymerization or block copolymerization. For example, in the type of an (A-B-A)-triblock copolymer, the structure can be $(A/C)-B-A$, $(A/C)-B-(A/C)$, $C-A-B-A$, $C-A-B-A-C$, $A-(B/C)-A$,

A-B-C-A, and A-C-B-A. In these expressions, (A/C) means that the block A contains the functional group C, and (B/C) means that the block B contains the acid anhydride group (C).

[0031]

The number-average molecular weight of the acrylic block copolymer (a) is not particularly limited and may be determined according to the required molecular weights of the methacrylic polymer block (A) and the acrylic polymer block (B). When the molecular weight is small, the block copolymer (a) may exhibit insufficient mechanical properties as an elastomer, while when the molecular weight is excessively large, processing characteristics may deteriorate. From this viewpoint, the number-average molecular weight of the acrylic block copolymer is preferably 30,000 to 500,000, more preferably 40,000 to 400,000, and most preferably 50,000 to 300,000.

[0032]

Although the ratio (M_w/M_n) of the weight-average molecular weight (M_w) to the number-average molecular weight (M_n) of the acrylic block copolymer (a) according to gel permeation chromatographic measurement is not particularly limited, the ratio is preferably 1 to 1.8, and more preferably 1 to 1.5. With the ratio (M_w/M_n) over 1.8, the uniformity of the acrylic block copolymer may deteriorate.

[0033]

The composition ratios of the methacrylic polymer block (A) and the acrylic polymer block (B) which constitute the acrylic block copolymer (a) are not particularly limited. The ratios may be determined according to the physical properties required for intended purposes, the moldability required for processing compositions, and the required molecular weights of the methacrylic polymer block (A) and the acrylic polymer block (B). For example, the composition ratios of the methacrylic polymer block (A) and the acrylic polymer block (B) are preferably 5% by weight to 80% by weight and 95% by weight to 20% by weight, more preferably 10% by weight to 60% by weight and 90% by weight to 40% by weight, and most preferably 20% by weight to 50% by weight and 80% by weight to 50% by weight, respectively. When the ratio of the methacrylic polymer block (A) is less than 5% by weight, rubber elasticity at high temperatures may decrease, while when the ratio exceeds 80% by weight, the mechanical properties of elastomers, particularly breaking elongation, may decrease, or the flexibility of compositions with thermoplastic resins may decrease.

[0034]

Assuming that the glass transition temperatures of the methacrylic polymer block (A) and the acrylic polymer block (B) which constitute the acrylic block copolymer (a) are T_{gA} and T_{gB} , respectively, the glass transition temperatures of

the methacrylic polymer block (A) and the acrylic polymer block (B) preferably satisfies the following relationship:

$$Tg_A > Tg_B$$

[0035]

The glass transition temperature (T_g) of each of the methacrylic polymer block (A) and the acrylic polymer block (B) can be determined using the weight ratio of the monomer of each polymer block according to the following Fox's equation:

[0036]

$$1/T_g = (W_1/T_{g1}) + (W_2/T_{g2}) + \dots + (W_m/T_{gm})$$

$$W_1 + W_2 + \dots + W_m = 1$$

In the equation, T_g represents the glass transition temperature of a polymer, T_{g1} , T_{g2} , ..., T_{gm} each represent the glass transition temperature of a homopolymer of each monomer, and W_1 , W_2 , ..., W_m each represent the weight ratio of each monomer.

[0037]

As the glass transition temperature of each homopolymer in the above Fox's equation, for example, the value described in Polymer Handbook Third Edition (Wiley-Interscience 1989) may be used.

[0038]

The glass transition temperature can be determined by DSC (differential scanning calorimetry) or a $\tan \delta$ peak of

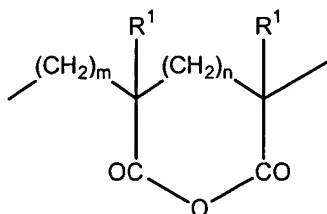
dynamic viscoelasticity. However, when the polarities of the methacrylic polymer block (A) and the acrylic polymer block (B) are excessively close to each other, or when the number of the polymerized monomers of a block is excessively small, the measured value may deviate from the value calculated according to the Fox's equation.

[0039]

The acid anhydride group (C) represented by formula (1) may be introduced into the block copolymer by any desired method without limitation.

[0040]

[Chem. 6]



[0041]

(wherein R¹s each represent a hydrogen atom or a methyl group and may be the same or different, n represents an integer of 0 to 3, and m represents an integer of 0 or 1.) However, from the viewpoint of easy introduction and easy purification after introduction, the acid anhydride group (C) is preferably introduced in the form of a functional group which is a precursor of the acid anhydride group (C)

into the acrylic block copolymer and then subjected to cyclization.

[0042]

In formula (1), n is an integer of 0 to 3, preferably 0 or 1, and more preferably 1. When n is 3 or more, polymerization tends to be complicated, or cyclization of the acid anhydride group tends to become difficult.

[0043]

In formula (1), m is an integer of 0 or 1. When n is 0, m is preferably 0, and when n is 1 to 3, m is preferably 1.

[0044]

The acid anhydride group (C) may be introduced in one or both of the methacrylic polymer block (A) and the acrylic polymer block (B). The acid anhydride group (C) may be introduced according to purposes, i.e., according to the reactive site of the acrylic block copolymer (a), cohesive force and glass transition temperatures of the blocks which constitute the acrylic block copolymer (a), and the required physical properties of the acrylic block copolymer (a). For example, when the methacrylic polymer block (A) or the acrylic polymer block (B) is desired to be selectively modified or reacted with a compound having an amino group or hydroxyl group using the acid anhydride group as a reactive site, the acid anhydride group (c) may be introduced into a block which is desired to be modified or reacted. In view

of improvement in the heat resistance and thermal decomposition resistance of the acrylic block copolymer (a), the acid anhydride group (C) may be introduced into the methacrylic polymer block (A). From the viewpoint that rubber elasticity is imparted to the acrylic block copolymer (a), the acid anhydride group (C) may be introduced as a cross-linking reactive site (cross-linking point) into the acrylic polymer block (B). As a nonlimiting example, the acid anhydride group (C) is preferably introduced into any one of the methacrylic polymer block (A) and the acrylic polymer block (B) from the viewpoint of control of the reactive site, heat resistance, and rubber elasticity. As a nonlimiting example, when the acid anhydride group (C) is introduced into the methacrylic polymer block (A), both R^1 s in formula (1) are preferably methyl groups, and when the acid anhydride group (C) is introduced into the acrylic polymer block (B), both R^1 s in formula (1) are preferably hydrogen atoms. Where both R^1 s are hydrogen atoms when the acid anhydride group is introduced into the methacrylic polymer block (A), and both R^1 s are methyl groups when the acid anhydride group is introduced into the acrylic polymer block (B), a polymerization operation for the acrylic block polymer (a) becomes complicated, and a difference between the glass transition temperatures of the methacrylic polymer block (A) and the acrylic polymer block (B) tends to

decrease to decrease the rubber elasticity of the acrylic block copolymer (a).

[0045]

A preferred range of the content of the acid anhydride group (C) depends on the cohesive force and reactivity of the acid anhydride group (C), the structure and composition of the acrylic block copolymer (a), the number of the constituent blocks of the acrylic block copolymer (a), and the glass transition temperatures thereof, and the introduction site and form of the acid anhydride group (C). For example, the content of the acid anhydride group (C) preferably ranges from 0.1% by weight or more and more preferably ranges from 0.5% by weight or more, relative to the whole of the acrylic block copolymer (a). With the content of less than 0.1% by weight, the reactivity of the acrylic block copolymer (a) and compatibility with thermoplastic resins tend to become insufficient. When the acid anhydride group (C) having high T_g is introduced into the methacrylic polymer block (A) serving as the hard segment in order to improve the heat resistance of the acrylic block copolymer (a), with the content of less than 0.1% by weight, the heat resistance may be not sufficiently improved to decrease the expression of rubber elasticity at high temperatures.

[0046]

The block containing the acid anhydride group (C) and the content of the acid anhydride group (C) may be appropriately determined according to the required reactivity, reactive site, cohesive force, and glass transition temperature.

[0047]

From the viewpoint of further improvement in heat resistance and cohesive force, the acrylic block copolymer (a) may contain the carboxyl group (D). The carboxyl group (D) can be produced in the process for introducing the acid anhydride group (C) into the acrylic block copolymer (a).

[0048]

The carboxyl group (D) may be introduced into only one or both of the methacrylic polymer block (A) and the acrylic polymer block (B). In view of the reactive site of the acrylic block copolymer (a), the cohesive force and glass transition temperatures of the constituent blocks of the acrylic block copolymer (a), and the required physical properties of the acrylic block copolymer (a), the carboxyl group (D) may be appropriately introduced according to purposes. As a nonlimiting example, from the viewpoint of control of the reactive site of the acrylic block copolymer (a) and ease of introduction of the carboxyl group (D) into the acrylic block copolymer (a), the carboxyl group (D) is preferably introduced into the block containing the acid

anhydride group (C). From the viewpoint of heat resistance and cohesive force, the carboxyl group (D) is more preferably introduced into the methacrylic polymer block (A). This is because when the carboxyl group (D) having high T_g and high cohesive force is introduced into the hard segment, the rubber elasticity can be further expressed even at a high temperature. In view of compatibility with the thermoplastic resin and/or the thermoplastic elastomer, the carboxyl group (D) is preferably introduced into the acrylic polymer block (B).

The number of the carboxyl group (D) per polymer block may be at least one. When the number is 2 or more, polymerization of a monomer containing the carboxyl group (D) may be random copolymerization or block copolymerization. For example, in the type of an (A1-B1-A1)-triblock copolymer, the structure can be (A1/D)-B1-A1, (A1/D)-B1-(A1/D), D-A1-B1-A1, D-A1-B1-A1-D, A1-(B1/D)-A1, A1-B1-D-A1, and A1-D-B1-D-A1. In these expressions, (A1/D) means that the block A1 contains the carboxyl group D, and (B1/D) means that the block B1 contains the carboxyl group D. Since the acid anhydride group (C) is also contained, A1 represents the methacrylic polymer block in which the acid anhydride group is introduced in a random form or block form, and B1 represents the acrylic polymer block in which the acid anhydride group is introduced in a random form or block form.

In the block A1 or B1, the segment and form in which the carboxyl group (D) is contained may be freely determined according to purposes.

[0049]

A preferred range of contents of the carboxyl group (D) depends on the cohesive force of the carboxyl group (D), the structure and composition of the acrylic block copolymer (a), the number of the constituent blocks of the acrylic block copolymer (a), and the introduction segment and form of the carboxyl group (D).

[0050]

For example, the content of the carboxyl group (D) preferably ranges from 0.1 to 50% by weight and more preferably 0.5 to 40% by weight, of the constituent monomers of the acrylic block copolymer (a). When the acrylic block copolymer (a) is required to have higher heat resistance and cohesive force, the carboxyl group (D) is preferably introduced within a range to 50% by weight. With the content of over 50% by weight, the carboxyl group (D) tends to cyclize with an adjacent ester unit at a high temperature, and thus the operation for introducing the carboxyl group (D) tends to become complicated. When less than 0.1% by weight of the carboxyl group (D) is introduced into the hard segment, heat resistance and cohesive force may be not sufficiently improved. The content of the carboxyl group

(D) is represented by percent by weight of a monomer originally containing the carboxyl group (D).

[0051]

<Methacrylic polymer block (A)>

From the viewpoint of easy production of the acrylic block copolymer having desired physical properties, cost, and availability, the constituent monomers of the methacrylic polymer block (A) include a methacrylate, a monomer having the acid anhydride group (C) and the carboxyl group (D), and 0 to 50% by weight, preferably 0 to 25% by weight, of another vinyl monomer copolymerizable therewith. When the content of the methacrylate is excessively low, the characteristics of the methacrylate, for example, the weather resistance, high glass transition temperature, and compatibility with resins, tend to deteriorate.

[0052]

The required molecular weight of the methacrylic polymer block (A) may be determined according to the required cohesive force of the methacrylic polymer block (A) and the time required for polymerization therefor.

[0053]

The cohesive force is considered to depend on molecular interaction (i.e., polarity) and a degree of entanglement. As the molecular weight increases, the number of entanglement points increases to increase the cohesive force.

Namely, assuming that the required molecular weight of the methacrylic polymer block (A) is M_A , and the molecular weight between entanglement points of the constituent polymer of the methacrylic polymer block (A) is Mc_A , a preferred example of the M_A range is $M_A > Mc_A$ when cohesive force is required, and $M_A > 2Mc_A$ when higher cohesive force is required. When a moderate degree of cohesive force and a creeping property are simultaneously satisfied, the M_A range is preferably $Mc_A < M_A < 2Mc_A$. As the molecular weight between entanglement points, the value described in the document by Wu, et al. (Polym. Eng. and Sci., 1990, vol. 30, p. 753) may be referred. For example, on the assumption that the methacrylic polymer block (A) entirely includes methyl methacrylate, when the cohesive force is required, a preferred example of the number-average molecular weight of the methacrylic polymer block (A) is in a range of 9200 or more. However, when the acid anhydride group (C) is introduced into the methacrylic polymer block (A), the cohesive force is imparted by the acid anhydride group (C), and thus the molecular weight can be set to a lower value. Since the polymerization time tends to increase as the number-average molecular weight increases, the number-average molecular weight may be determined according to the required productivity. However, the number-average molecular weight is preferably 200,000 or less, and more

preferably 100,000 or less. However, when the acid anhydride group (C) is introduced into the methacrylic polymer block (A), the cohesive force is imparted by the acid anhydride group (C), and thus the molecular weight can be set to a lower value.

[0054]

Examples of the constituent methacrylate of the methacrylic polymer block (A) include methacrylic acid aliphatic hydrocarbon (for example, alkyl) esters, such as methyl methacrylate, ethyl methacrylate, n-propyl methacrylate, n-butyl methacrylate, isobutyl methacrylate, n-pentyl methacrylate, n-hexyl methacrylate, n-heptyl methacrylate, n-octyl methacrylate, 2-ethylhexyl methacrylate, nonyl methacrylate, decyl methacrylate, dodecyl methacrylate, and stearyl methacrylate; methacrylic acid alicyclic hydrocarbon esters, such as cyclohexyl methacrylate and isobornyl methacrylate; methacrylic acid aralkyl esters, such as benzyl methacrylate; methacrylic acid aromatic hydrocarbon esters, such as phenyl methacrylate and toluyl methacrylate; methacrylic acid esters with functional group-containing alcohols having ether oxygen, such as 2-methoxyethyl methacrylate and 3-methoxybutyl methacrylate; and methacrylic acid fluoroalkyl esters, such as trifluoromethyl methacrylate, 2-trifluoroethyl methacrylate, 2-perfluoroethylethyl

methacrylate, 2-perfluoroethyl-2-perfluorobutylethyl methacrylate, 2-perfluoroethyl methacrylate, perfluoromethyl methacrylate, diperfluoromethylmethyl methacrylate, 2-perfluoromethyl-2-perfluoroethylmethyl methacrylate, 2-perfluorohexylethyl methacrylate, 2-perfluorodecylethyl methacrylate, and 2-perfluorohexadecylethyl methacrylate.

[0055]

These methacrylates are used alone or in combination of two or more. Among these methacrylates, methyl methacrylate is preferred from the viewpoint of compatibility with a thermoplastic resin to be combined, cost, and availability.

[0056]

Examples of the vinyl monomer copolymerizable with the constituent methacrylate of the methacrylic polymer block (A) include acrylates, aromatic alkenyl compounds, vinyl cyanide compounds, conjugated diene compounds, halogen-containing unsaturated compounds, unsaturated dicarboxylic acid compounds, vinyl ester compounds, and maleimide compounds.

[0057]

Examples of acrylates include acrylic acid aliphatic hydrocarbon (for example, alkyl) esters, such as methyl acrylate, ethyl acrylate, n-propyl acrylate, n-butyl acrylate, isobutyl acrylate, n-pentyl acrylate, n-hexyl acrylate, n-heptyl acrylate, n-octyl acrylate, 2-ethylhexyl

acrylate, nonyl acrylate, decyl acrylate, dodecyl acrylate, and stearyl acrylate; acrylic acid alicyclic hydrocarbon esters, such as cyclohexyl acrylate and isobornyl acrylate; acrylic acid aromatic hydrocarbon esters, such as phenyl acrylate and toluyll acrylate; acrylic acid aralkyl esters, such as benzyl acrylate; acrylic acid esters with functional group-containing alcohols having ether oxygen, such as 2-methoxyethyl acrylate and 3-methoxybutyl acrylate; and acrylic acid fluoroalkyl esters, such as trifluoromethylmethyl acrylate, 2-trifluoromethylethyl acrylate, 2-perfluoroethylethyl acrylate, 2-perfluoroethyl-2-perfluorobutylethyl acrylate, 2-perfluoroethyl acrylate, perfluoromethyl acrylate, diperfluoromethylmethyl acrylate, 2-perfluoromethyl-2-perfluoroethylmethyl acrylate, 2-perfluorohexylethyl acrylate, 2-perfluorodecylethyl acrylate, and 2-perfluorohexadecylethyl acrylate.

[0058]

Examples of aromatic alkenyl compounds include styrene, α -methylstyrene, p-methylstyrene, and p-methoxystyrene.

[0059]

Examples of vinyl cyanide compounds include acrylonitrile and methacrylonitrile.

[0060]

Examples of conjugated diene compounds include butadiene and isoprene.

[0061]

Examples of halogen-containing unsaturated compounds include vinyl chloride, vinylidene chloride, perfluoroethylene, perfluoropropylene, and vinylidene fluoride.

[0062]

Examples of unsaturated dicarboxylic acid compounds include maleic anhydride, maleic acid, maleic acid monoalkyl esters and dialkyl esters, fumaric acid, and fumaric acid monoalkyl esters and dialkyl esters.

[0063]

Examples of vinyl ester compounds include vinyl acetate, vinyl propionate, vinyl pivalate, vinyl benzoate, and vinyl cinnamate.

[0064]

Examples of maleimide compounds include maleimide, methylmaleimide, ethylmaleimide, propylmaleimide, butylmaleimide, hexylmaleimide, octylmaleimide, dodecylmaleimide, stearylmaleimide, phenylmaleimide, and cyclohexylmaleimide.

[0065]

These compounds are used alone or in combination of two or more. The vinyl monomer is preferably selected according to compatibility of the acrylic block copolymer with the thermoplastic resin and/or the thermoplastic elastomer. A

polymer of methyl methacrylate is depolymerized approximately quantitatively by thermal decomposition. However, in order to suppress depolymerization, the polymer can be copolymerized with an acrylate, for example, methyl acrylate, ethyl acrylate, butyl acrylate, 2-methoxyethyl acrylate, or a mixture thereof, or styrene. In order to further improve oil resistance, the polymer can be copolymerized with acrylonitrile.

[0066]

The glass transition temperature of the methacrylic polymer block (A) is preferably 100°C or more, and more preferably 110°C or more. With the glass transition temperature of less than 100°C, rubber elasticity at high temperatures degrades.

[0067]

The glass transition temperature (T_g) of the polymer (the methacrylic polymer block (A)) can be determined from the weight ratio of the monomer of each polymer segment according to the Fox's equation. The glass transition temperature is calculated according to the Fox's equation using the glass transition temperature of a homopolymer of each monomer which is described in Polymer Handbook Third Edition (Wiley-Interscience 1989).

[0068]

<Acrylic polymer block (B)>

The constituent monomers of the acrylic polymer block (B) preferably include an acrylate, a monomer containing the acid anhydride group (C) or the carboxyl group (D), and 0 to 50% by weight, preferably 0 to 25% by weight, of a vinyl monomer copolymerizable therewith from the viewpoint of easy production of a composition having desired physical properties, cost, and availability. When the ratio of the acrylate is less than 50% by weight, the physical properties of a composition, particularly impact resistance, which are characteristic of use of an acrylate, tend to deteriorate.

[0069]

The required molecular weight of the acrylic polymer block (B) may be determined according to the required elastic modulus and rubber elasticity of the acrylic polymer block (B), and the time required for polymerization therefor.

[0070]

The elastic modulus is closely related to the mobility of a molecular chain (i.e., glass transition temperature) and the molecular weight thereof, and the inherent elastic modulus is not exhibited unless the molecular weight is a certain value or more. This is true for rubber elasticity, but the molecular weight is preferably as large as possible from the viewpoint of rubber elasticity. For example, a range of the required molecular weight M_B of the block (B) is preferably $M_B > 3,000$, more preferably $M_B > 5,000$, further

preferably $M_B > 10,000$, particularly preferably $M_B > 20,000$, and most preferably $M_B > 40,000$. However, the polymerization time tends to increase as the number-average molecular weight increases, and thus the molecular weight is preferably 500,000 or less, and more preferably 300,000 or less according to the required productivity.

[0071]

Examples of the constituent acrylate of the acrylic polymer block (B) include acrylic acid aliphatic hydrocarbon (for example, alkyl) esters, such as methyl acrylate, ethyl acrylate, n-propyl acrylate, n-butyl acrylate, isobutyl acrylate, n-pentyl acrylate, n-hexyl acrylate, n-heptyl acrylate, n-octyl acrylate, 2-ethylhexyl acrylate, nonyl acrylate, decyl acrylate, dodecyl acrylate, and stearyl acrylate; acrylic acid alicyclic hydrocarbon esters, such as cyclohexyl acrylate and isobornyl acrylate; methacrylic acid aromatic hydrocarbon esters, such as phenyl acrylate and toluyl acrylate; acrylic acid aralkyl esters, such as benzyl acrylate; acrylic acid esters with functional group-containing alcohols having ether oxygen, such as 2-methoxyethyl acrylate and 3-methoxybutyl acrylate; and acrylic acid fluoroalkyl esters, such as trifluoromethylmethyl acrylate, 2-trifluoromethylethyl acrylate, 2-perfluoroethylethyl acrylate, 2-perfluoroethyl-2-perfluorobutylethyl acrylate, 2-perfluoroethyl acrylate,

perfluoromethyl acrylate, diperfluoromethylmethyl acrylate, 2-perfluoromethyl-2-perfluoroethylmethyl acrylate, 2-perfluorohexylethyl acrylate, 2-perfluorodecylethyl acrylate, and 2-perfluorohexadecylethyl acrylate. These acrylates are used alone or in combination of two or more.

[0072]

Among the acrylates, n-butyl acrylate is preferred from the viewpoint of impact resistance of a thermoplastic resin composition, cost, and availability. When the composition is required to have oil resistance, n-ethyl acrylate is preferred. When low-temperature characteristics are required, 2-ethylhexyl acrylate is preferred. When oil resistance and low-temperature characteristics are desired to be simultaneously satisfied, a mixture of n-ethyl acrylate, n-butyl acrylate, and 2-methoxyethyl acrylate is preferred.

[0073]

Examples of the vinyl monomer copolymerizable with the constituent acrylate of the acrylic polymer block (B) include methacrylates, aromatic alkenyl compounds, vinyl cyanide compounds, conjugated diene compounds, halogen-containing unsaturated compounds, unsaturated dicarboxylic acid compounds, vinyl ester compounds, and maleimide compounds.

[0074]

Examples of methacrylates include methacrylic acid aliphatic hydrocarbon (for example, alkyl) esters, such as methyl methacrylate, ethyl methacrylate, n-propyl methacrylate, n-butyl methacrylate, isobutyl methacrylate, n-pentyl methacrylate, n-hexyl methacrylate, n-heptyl methacrylate, n-octyl methacrylate, 2-ethylhexyl methacrylate, nonyl methacrylate, decyl methacrylate, dodecyl methacrylate, and stearyl methacrylate; methacrylic acid alicyclic hydrocarbon esters, such as cyclohexyl methacrylate and isobornyl methacrylate; methacrylic acid aralkyl esters, such as benzyl methacrylate; methacrylic acid aromatic hydrocarbon esters, such as phenyl methacrylate and toluyl methacrylate; methacrylic acid esters with functional group-containing alcohols having ether oxygen, such as 2-methoxyethyl methacrylate and 3-methoxybutyl methacrylate; and methacrylic acid fluoroalkyl esters, such as trifluoromethylmethyl methacrylate, 2-trifluoromethylethyl methacrylate, 2-perfluoroethylethyl methacrylate, 2-perfluoroethyl-2-perfluorobutylethyl methacrylate, 2-perfluoroethyl methacrylate, perfluoromethyl methacrylate, diperfluoromethylmethyl methacrylate, 2-perfluoromethyl-2-perfluoroethylmethyl methacrylate, 2-perfluorohexylethyl methacrylate, 2-perfluorodecylethyl methacrylate, and 2-perfluorohexadecylethyl methacrylate.

[0075]

Examples of aromatic alkenyl compounds include styrene, α -methylstyrene, p-methylstyrene, and p-methoxystyrene. Examples of vinyl cyanide compounds include acrylonitrile and methacrylonitrile.

[0076]

Examples of conjugated diene compounds include butadiene and isoprene.

[0077]

Examples of halogen-containing unsaturated compounds include vinyl chloride, vinylidene chloride, perfluoroethylene, perfluoropropylene, and vinylidene fluoride.

[0078]

Examples of unsaturated dicarboxylic acid compounds include maleic anhydride, maleic acid, maleic acid monoalkyl esters and dialkyl esters, fumaric acid, and fumaric acid monoalkyl esters and dialkyl esters.

[0079]

Examples of vinyl ester compounds include vinyl acetate, vinyl propionate, vinyl pivalate, vinyl benzoate, and vinyl cinnamate.

[0080]

Examples of maleimide compounds include maleimide, methylmaleimide, ethylmaleimide, propylmaleimide, butylmaleimide, hexylmaleimide, octylmaleimide,

dodecylmaleimide, stearylmaleimide, phenylmaleimide, and cyclohexylmaleimide.

[0081]

These compounds are used alone or in combination of two or more. The vinyl monomer is preferably selected according to the required glass transition temperature, elastic modulus, and polarity of the acrylic polymer block (B), the required physical properties of the composition, and compatibility with the thermoplastic resin and/or the thermoplastic elastomer. For example, the polymer block can be copolymerized with acrylonitrile, for further improving oil resistance of the composition.

[0082]

The glass transition temperature of the acrylic polymer block (B) is preferably 50°C or less, and more preferably 0°C or less. With the glass transition temperature of over 50°C, the rubber elasticity of the acrylic block copolymer (a) tends to degrade.

[0083]

The glass transition temperature (T_g) of the polymer (the acrylic polymer block (B)) can be determined from the weight ratio of the monomer of each polymer segment according to the Fox's equation. The glass transition temperature is calculated according to the Fox's equation using the glass transition temperature of a homopolymer of

each monomer, which is described in Polymer Handbook Third Edition (Wiley-Interscience 1989).

[0084]

<Acid anhydride group (C)>

The acid anhydride group (C) is characterized in that it has reactivity with a compound having an amino group, a hydroxyl group, or the like, and thus it can be used as a reactive site for modifying a polymer, as a site for improving compatibility in a blend with the thermoplastic resin and/or the thermoplastic elastomer, or as a cross-linking point for imparting higher rubber elasticity to a soft segment. Since the acid anhydride group (C) also has a high glass transition temperature (T_g), the acid anhydride group (C) has the effect of improving the heat resistance of the acrylic block copolymer (a) when being introduced into the hard segment. The glass transition temperature of a polymer containing an acid anhydride group is high, and for example, the glass transition temperature of polymethacrylic anhydride is as high as 159°C. By introducing a unit containing the acid anhydride, the heat resistance of the acrylic block copolymer can be improved.

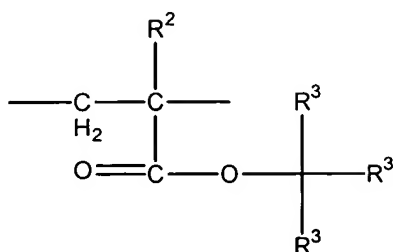
[0085]

As a method for introducing the acid anhydride group (C), preferably, a precursor of the acid anhydride group is introduced into the acrylic block copolymer and then

cyclized. As a nonlimiting example, the acid anhydride group is preferably introduced by melt-kneading cyclization of an acrylic block copolymer (d) at a temperature of 180°C to 300°C, the block copolymer (d) containing at least one unit represented by formula (2):

[0086]

[Chem. 7]



[0087]

(wherein R² represents a hydrogen atom or a methyl group, and R³s each represent a hydrogen atom, a methyl group, or a phenyl group and may be the same or different as long as at least one of R³s is a methyl group).

[0088]

The unit represented by formula (2) can be introduced into the acrylic block copolymer (d) by copolymerization with an acrylate or methacrylate which can form the unit represented by formula (2).

[0089]

The unit represented by formula (2) undergoes elimination and cyclization with the adjacent ester unit at

a high temperature to produce an acid anhydride group (refer to, for example, Hatada, et al., J. M. S.-PURE APPL. CHEM., A30 (9&10), PP. 645-667 (1993)). According to this document, a polymer having a bulk ester unit and β -hydrogen generally undergoes decomposition of the ester unit and then cyclization at a high temperature to produce an acid anhydride group. By using this method, the acid anhydride group can easily be introduced into the acrylic block copolymer (a). Specific examples of such a monomer include, without limitation to, tert-butyl acrylate, isopropyl acrylate, α,α -dimethylbenzyl acrylate, α -methylbenzyl acrylate, tert-butyl methacrylate, isopropyl methacrylate, α,α -dimethylbenzyl methacrylate, and α -methylbenzyl methacrylate. Among these monomers, tert-butyl acrylate and tert-butyl methacrylate are preferred from the viewpoint of availability, easy polymerization, and easy production of the acid anhydride group.

[0090]

In order to form the acid anhydride group, the copolymer (d) is preferably heated at a high temperature. As a nonlimiting example, heating is preferably performed at 180°C to 300°C. With heating at a temperature of lower than 180°C, the acid anhydride group may be not sufficiently produced, while with heating at a temperature of over 300°C, the polymer (d) may be decomposed.

[0091]

<Carboxyl group (D)>

The carboxyl group (D) has high cohesive force, and a monomer containing a carboxyl group has a high glass transition temperature (T_g) and thus has the effect of improving the heat resistance of the acrylic block copolymer. Although a functional group such as a hydroxyl group also has a hydrogen bonding ability, the functional group has low T_g and has the small effect of improving heat resistance, as compared with a monomer containing a carboxyl group. Therefore, from the viewpoint of further improvements in heat resistance and cohesive force of the acrylic block copolymer, the acrylic block copolymer may contain the carboxyl group (D).

[0092]

A method for introducing the carboxyl group (D) is not particularly limited, but the carboxyl group (D) is preferably produced in the process for introducing the acid anhydride group (C) into the acrylic block copolymer (a) in view of easy introduction.

[0093]

The method will be described below.

[0094]

In the method producing the carboxyl group (D) in the process for introducing the acid anhydride group (C) into

the acrylic block copolymer (a), the acrylic block copolymer (d) containing the unit represented by formula (2) is heated at 180°C to 300°C to introduce the acid anhydride group (C). However, the carboxyl group (D) can be introduced by controlling the heating temperature and time and the content of the unit represented by formula (2). The unit represented by formula (2) undergoes elimination and cyclization with the adjacent ester unit at a high temperature to produce the acid anhydride group (refer to, for example, Hatada, et al., J. M. S.-PURE APPL. CHEM., A30 (9&10), PP. 645-667 (1993)). In this case, the ester units partially take a cyclization path including decomposition of the ester unit to produce the carboxyl group, and then cyclization to produce the acid anhydride group. By utilizing this path, the carboxyl group (D) can be introduced by appropriately controlling the heating temperature and time according to the type and content of the unit represented by formula (2). The carboxyl group (D) tends to cyclize with the adjacent ester unit at a high temperature. Therefore, when over 50% by weight of the carboxyl group (D) is introduced, an introduction operation tends to become complicated.

[0095]

A polymer having the carboxyl group has a high glass transition temperature, and for example, polymethacrylic

acid has a glass transition temperature of as high as 228°C. Therefore, the heat resistance of the acrylic block copolymer can be improved by introducing a monomer constituting such a polymer.

[0096]

<Process for producing the acrylic block copolymer (d)>

Although the process for producing the acrylic block copolymer (d) is not particularly limited, controlled polymerization using a initiator for polymerization is preferably performed. Examples of the controlled polymerization include living anionic polymerization, radical polymerization using a chain transfer agent, and living radical polymerization recently developed. In particular, living radical polymerization is preferred from the viewpoint of control of the molecular weight and structure of the acrylic block copolymer.

[0097]

The living radical polymerization is radical polymerization in which the activity of the polymerization terminal is maintained without a loss. In a narrow sense, living polymerization represents polymerization in which the terminal continuously possesses activity. However, living polymerization generally includes pseudo living polymerization in which inactivated terminals are equilibrium with activated terminals. In the present

invention, the meaning of living polymerization includes the pseudo living polymerization. In recent years, living radical polymerization has been actively studied by various groups.

[0098]

Examples of living radical polymerization include polymerization using a polysulfide as a chain transfer agent, polymerization using a cobalt porphyrin complex (Journal of American Chemical Society (J. Am. Chem. Soc.), 1994, vol. 116, p. 7943) or a nitroxide compound as a radical scavenger (Macromolecules, 1994, vol. 27, p. 7228), and atom transfer radical polymerization (ATRP) using an organic halide as an initiator and a transition metal complex as a catalyst. In the present invention, any one of these polymerization methods can be used, but atom transfer radical polymerization is preferred from the viewpoint of ease of control.

[0099]

The atom transfer radical polymerization is performed using an organic halide or a sulfonyl halide compound as an initiator, and using a metal complex including a central metal selected from the elements of Groups VIII, IX, X, or XI of the periodic table as a catalyst (refer to, for example, Matyjaszewski, et al., J. Am. Chem. Soc., 1995, Vol. 117, p. 5614, Macromolecules, 1995, Vol. 28, p. 7901,

Science, 1996, Vo. 272, p. 866, or Sawamoto, et al.,
Macromolecules, 1995, Vol. 28, p. 1721).

[0100]

A radical polymerization method generally has a very high polymerization rate and easily causes termination reaction such as coupling between radicals or the like. However, in the above-mentioned method, polymerization proceeds in a living state to produce a polymer having a narrow molecular weight distribution ($M_w/M_n = 1.1$ to 1.5), and the molecular weight can be freely controlled by the changing ratio of the monomer to the initiator.

[0101]

In the atom transfer radical polymerization, a mono-, di- or higher-functional compound can be used as the organic halide or the sulfonyl halide compound serving as the initiator. These compounds may be appropriately used according to purposes. However, a monofunctional compound is preferably used for producing a diblock copolymer from the viewpoint of availability of the initiator, and a difunctional compound is preferably used for producing a (A-B-A)-triblock copolymer or (B-A-B)-triblock copolymer from the viewpoint of the number of the reaction steps and the short reaction time. A polyfunctional compound is preferably used for producing a branched block copolymer from the viewpoint of the number of the reaction steps and

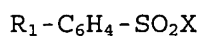
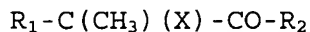
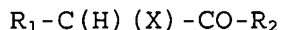
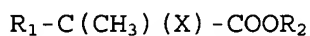
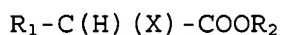
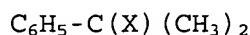
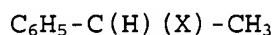
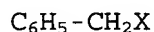
the short reaction time.

[0102]

A macroinitiator can be used as the initiator. The macroinitiator is a compound among the organic halide and the sulfonyl halide compound, and includes a polymer having a halogen atom bonded to an end of its molecular chain. Such a polymeric initiator can be produced by a controlled polymerization method other than the living radical polymerization method, and is thus characteristic in that a block copolymer including polymers bonded together and produced by different polymerization methods can be produced.

[0103]

Examples of the monofunctional compound include the following:



[0104]

In the formulae, C_6H_5 represents a phenyl group, C_6H_4 represents a phenylene group (which may be any one of ortho-

substituted, metha-substituted, and para-substituted), R^1 represents a hydrogen atom, an alkyl group having 1 to 20 carbon atoms, an aryl group having 6 to 20 carbon atoms, or an aralkyl group having 7 to 20 carbon atoms, X represents chlorine, bromine, or iodine, and R^2 represents a monovalent organic group having 1 to 20 carbon atoms.

[0105]

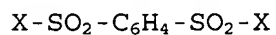
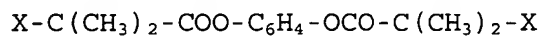
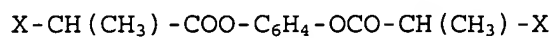
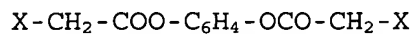
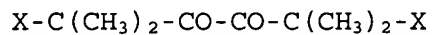
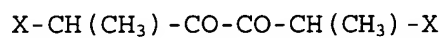
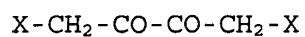
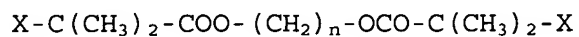
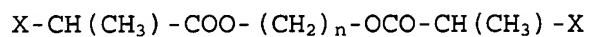
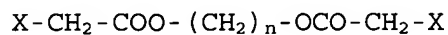
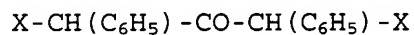
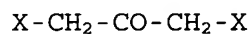
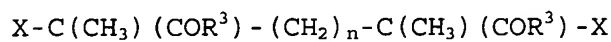
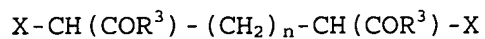
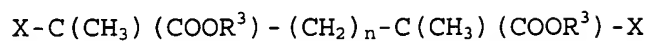
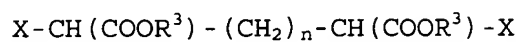
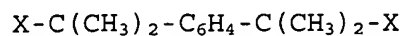
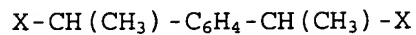
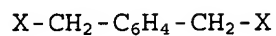
Examples of an alkyl group (including an alicyclic hydrocarbon group) having 1 to 20 carbon atoms as R^1 include methyl, ethyl, propyl, isopropyl, n-butyl, isobutyl, tert-butyl, n-pentyl, n-hexyl, cyclohexyl, n-heptyl, n-octyl, 2-ethylhexyl, nonyl, decyl, dodecyl, and isobornyl. Examples of an aryl group having 6 to 20 carbon atoms include phenyl, toluy, and naphthyl. Examples of an aralkyl group having 7 to 20 carbon atoms include benzyl and phenetyl.

[0106]

Specific examples of the monofunctional compound include tosyl bromide, methyl 2-bromopropionate, ethyl 2-bromopropionate, butyl 2-bromopropionate, methyl 2-bromoisobutyrate, ethyl 2-bromoisobutyrate, and butyl 2-bromoisobutyrate. Among these compounds, ethyl 2-bromopropionate and butyl 2-bromopropionate are preferred from the viewpoint that polymerization can easily be controlled because the structures are similar to that of an acrylate monomer.

[0107]

Examples of the difunctional compound include the following:



[0108]

In the formulae, R^3 represents alkyl having 1 to 20 carbon atoms, aryl having 6 to 20 carbon atoms, or aralkyl having 7 to 20 carbon atoms, and n represents an integer of 0 to 20. C_6H_5 , C_6H_4 , and X represent the same as the above.

[0109]

Specific examples of alkyl having 1 to 20 carbon atoms, aryl having 6 to 20 carbon atoms, and aralkyl having 7 to 20 carbon atoms as R^3 are the same as those of alkyl having 1 to 20 carbon atoms, aryl having 6 to 20 carbon atoms, and aralkyl having 7 to 20 carbon atoms as R^1 . Therefore, description thereof is omitted.

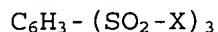
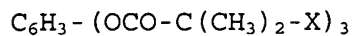
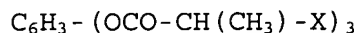
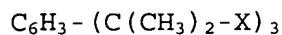
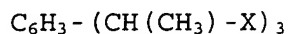
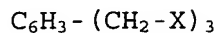
[0110]

Specific examples of the difunctional compound include bis(bromomethyl)benzene, bis(1-bromoethyl)benzene, bis(1-bromoisopropyl)benzene, dimethyl 2,3-dibromosuccinate, diethyl 2,3-dibromosuccinate, dibutyl 2,3-dibromosuccinate, dimethyl 2,4-dibromoglutarate, diethyl 2,4-dibromoglutarate, dibutyl 2,4-dibromoglutarate, dimethyl 2,5-dibromoadipate, diethyl 2,5-dibromoadipate, dibutyl 2,5-dibromoadipate, dimethyl 2,6-dibromopimelate, diethyl 2,6-dibromopimelate, dibutyl 2,6-dibromopimelate, dimethyl 2,7-dibromosuberate, diethyl 2,7-dibromosuberate, and dibutyl 2,7-dibromosuberate. Among these compounds, bis(bromomethyl)benzene, diethyl 2,5-dibromoadipate, and diethyl 2,6-dibromopimelate are preferred from the viewpoint of availability of raw

materials.

[0111]

Examples of the polyfunctional compound include the following:



[0112]

In the formulae, C_6H_3 represents a trivalent phenyl group (having any desired combination of three bonding positions among the 1- to 6-position), and X represents the same as the above.

[0113]

Specific examples of the polyfunctional group include tris(bromomethyl)benzene, tris(1-bromoethyl)benzene, and tris(1-bromoisopropyl)benzene. Among these compounds, tris(bromomethyl)benzene is preferred from the viewpoint of availability of raw materials.

[0114]

When an organic halide or sulfonyl halide compound having a functional group other than a polymerization

initiating group is used, a polymer having a functional group other than a polymerization initiating group in its terminal or its molecule can be obtained. Examples of a functional group other than a polymerization initiating group include alkenyl, hydroxyl, epoxy, amino, amido, and silyl.

[0115]

The organic halide or sulfonyl halide compound which can be used as the initiator has a carbon atom bonded to a halogen group (halogen atom) and to a carbonyl or phenyl group, and a carbon-halogen bond is activated to initiate polymerization. The amount of the initiator used may be determined from a molar ratio to the monomer used according to the required molecular weight of the acrylic block copolymer. Namely, the molecular weight of the acrylic block copolymer can be controlled by controlling the number of the monomer molecules used per molecule of the initiator.

[0116]

Although the transition metal complex used as the catalyst for the atom transfer radical polymerization is not particularly limited, complexes of mono- or zero-valent copper, divalent ruthenium, divalent iron, and divalent nickel are preferably used.

[0117]

Among these complexes, copper complexes are preferred

from the viewpoint of cost and reaction controllability. Examples of copper(I) compounds include cuprous chloride, cuprous bromide, cuprous iodide, cuprous cyanide, cuprous oxide, and cuprous perchlorate. Among these compounds, cuprous chloride and cuprous bromide are preferred from the viewpoint of polymerization controllability. When a copper(I) compound is used, a ligand may be added for increasing catalytic activity. Examples of such a ligand include 2,2'-bipyridyl compounds such as 2,2'-bipyridyl and its derivatives (for example, 4,4'-dinoryl-2,2'-bipyridyl and 4,4'-di(5-noryl)-2,2'-bipyridyl); 1,10-phenanthroline compounds such as 1,10-phenanthroline and its derivatives (for example, 4,7-dinoryl-1,10-phenanthroline and 5,6-dinoryl-1,10-phenanthroline); and polyamines such as tetramethyldiethylenetriamine (TMEDA), pentamethyldiethylenetriamine, and hexamethyl(2-aminoethyl)amine.

[0118]

Also, a tris(triphenylphosphine) complex ($\text{RuCl}_2(\text{PPh}_3)_3$) of ruthenium(II) chloride is preferred as the catalyst. When a ruthenium compound is used as the catalyst, an aluminum alkoxide may be added as an activating agent. Furthermore, a bis(triphenylphosphine) complex ($\text{FeCl}_2(\text{PPh}_3)_2$) of divalent iron, a bis(triphenylphosphine) complex ($\text{NiCl}_2(\text{PPh}_3)_2$) of divalent nickel, and a bis(tributylphosphine) complex

($\text{NiBr}_2(\text{PBU}_3)_2$) of divalent nickel are preferred as the catalyst.

[0119]

Although the types of the catalyst, ligand, and activating agent used are not particularly limited, the types may be properly determined from the relation between the required reaction rate and the types of the initiator, monomer, and solvent used. For example, when an acrylic monomer such as an acrylate or the like is used for polymerization, a propagation end of a polymer chain preferably has a carbon-bromine bond from the controllability of polymerization. Therefore, preferably, an organic bromide or sulfonyl bromide is used as the initiator, acetonitrile is used as the solvent, a metal complex including copper or copper bromide, preferably cuprous bromide, as a central metal is used as the catalyst, and pentamethyldiethylenetriamine or the like is used as the ligand. On the other hand, when a methacrylic monomer such as a methacrylate or the like is used for polymerization, a propagation end of a polymer chain preferably has a carbon-chlorine bond from the controllability of polymerization. Therefore, preferably, an organic chloride or sulfonyl chloride is used as the initiator, acetonitrile, and if required, a mixture with toluene, is used as the solvent, a metal complex including copper or copper chloride,

preferably cuprous chloride, as a central metal is used as the catalyst, and pentamethyldiethylenetriamine or the like is used as the ligand.

[0120]

The amounts of the catalyst and ligand used may be properly determined from the relation between the required reaction rate and the amounts of the initiator, monomer, and solvent used. For example, when a polymer having a high molecular weight is desired, the initiator/monomer ratio must be lower than that for producing a polymer having a low molecular weight. In this case, the reaction rate can be increased by increasing the amounts of the catalyst and ligand used. Also, when a polymer having a higher glass transition temperature than room temperature is produced, in some cases, an appropriate organic solvent is added for decreasing the viscosity of the system and increasing the efficiency of stirring, and thus the reaction rate tends to decrease. In this case, the reaction rate can be increased by increasing the amounts of the catalyst and ligand used.

[0121]

The atom transfer radical polymerization can be performed without a solvent (bulk polymerization) or in any of various solvents. The bulk polymerization or polymerization in any of various solvents can be stopped during the reaction.

[0122]

Examples of the solvent include hydrocarbon solvents, ether solvents, halogenated hydrocarbon solvents, ketone solvents, alcohol solvents, nitrile solvents, ester solvents, and carbonate solvents.

[0123]

Examples of hydrocarbon solvents include benzene and toluene. Examples of ether solvents include diethyl ether and tetrahydrofuran. Examples of halogenated hydrocarbon solvents include methylene chloride and chloroform. Examples of ketone solvents include acetone, methyl ethyl ketone, and methyl isobutyl ketone. Examples of alcohol solvents include methanol, ethanol, propanol, isopropanol, n-butanol, and tert-butanol. Examples of nitrile solvents include acetonitrile, propionitrile, and benzonitrile. Examples of ester solvents include ethyl acetate and butyl acetate. Examples of carbonate solvents include ethylene carbonate and propylene carbonate.

[0124]

These solvents may be used alone or in combination of two or more.

[0125]

When the solvent is used, the amount of the solvent used may be properly determined based on the relation between the viscosity of the whole system and the required

efficiency of stirring (i.e., reaction rate). When bulk polymerization or polymerization in a solvent is stopped during the reaction, the conversion rate of the monomer at the reaction stop point may be properly determined based on the relation between the viscosity of the whole system and the required efficiency of stirring (i.e., reaction rate).

[0126]

The polymerization can be performed in the range of room temperature to 200°C and preferably 50°C to 150°C.

[0127]

Examples of a method for producing the acrylic block copolymer by the above-described polymerization include a method of successively adding monomers, a method of polymerizing a monomer for a second block using a previously synthesized polymer as a macroinitiator, and a method of bonding different polymers by reaction, the polymers being separately produced by polymerization. Any one of these methods may be properly used according to purposes. In view of simplicity of the production process, the method of successively adding monomers is preferably used. When it is desired to avoid a remaining monomer of a first block from being copolymerized with a second block, the method of polymerizing a monomer of the second block using the previously synthesized polymer as the macroinitiator is preferably used.

[0128]

Detailed description will be made of the method of successively adding monomers, and the method of polymerizing a monomer of the second block using the previously synthesized polymer as the macroinitiator. However, the method for producing the acrylic block copolymer of the present invention is not limited to these methods.

[0129]

In the method of successively adding monomers, the second monomer to be polymerized is preferably charged when the conversion ratio of the first monomer to be polymerized reaches 80% to 95%. When polymerization proceeds until the conversion ratio exceeds 95% (e.g., 96% to 100%), the propagation reaction of a polymer chain is inhibited with high probability. There is also the tendency that polymer radicals readily react with each other to easily cause side reactions such as disproportionation, coupling, chain transfer, and the like. When the second monomer to be polymerized is charged at a conversion ratio of less than 80% (e.g., 79% or less), the first monomer to be polymerized may be disadvantageously mixed and copolymerized with the second monomer to be polymerized.

[0130]

In this case, possible methods for adding in order the monomers include a method (x1) in which an acrylic monomer

is first charged and polymerized, and then a methacrylic monomer is charged and polymerized, and a method (y1) in which a methacrylic monomer is first charged and polymerized, and then an acrylic monomer is charged and polymerized. The method (x1) in which an acrylic monomer is first charged and polymerized, and then a methacrylic monomer is charged and polymerized is preferred from the viewpoint of controllability of polymerization. This is because it is preferable that the methacrylic polymer block is propagated from the end of the acrylic polymer block.

[0131]

As a possible example of the method of polymerizing a monomer of the second block using the previously synthesized polymer as the macroinitiator, polymerization of a monomer of the first block is stopped at a desired point by decreasing the temperature in a living state, and a monomer of the second block is added after the monomer of the first block is removed by distillation or the like under reduced pressure. When polymerization of monomer of a third block is desired, the same operation as that for the second block may be performed. This method can avoid the remaining monomer of the previous block from being copolymerized in polymerization of a monomer of the subsequent block.

[0132]

In this case, possible methods for polymerizing in

order the monomers of the blocks include a method (x2) in which an acrylic block is first produced by polymerization, and then a methacrylic block is produced by polymerization, and a method (y2) in which a methacrylic block is produced by polymerization, and then an acrylic block is produced by polymerization. The method (x2) in which an acrylic block is first produced by polymerization, and then a methacrylic block is produced by polymerization is preferred from the viewpoint of controllability of polymerization. This is because it is preferable that the methacrylic polymer block be propagated from the end of the acrylic polymer block.

[0133]

Next, a method for determining the conversion ratio of the acrylic monomer, the methacrylic monomer, or the like will be described. In order to determine the conversion ratio, a gas chromatographic (GC) method, a weight method, or the like can be used. In the GC method, reaction solutions are sampled from the polymerization system before initiation of the reaction and any time in the course of the reaction and subjected to GC measurement, and the consumption rate of a monomer is determined from the existence ratio of the monomer to the internal standard previously added to the polymerization system. This method is advantageous in that even when a plurality of monomers is present in the system, the conversion ratios can be

independently determined. In the weight method, a reaction solution is sampled from the polymerization system, and a solid concentration is determined from the weights before and after drying to determine the overall conversion ratio of monomers. This method is advantageous in that the conversion ratio can easily be determined. Of these methods, the GC method is preferred for a case in which a plurality of monomers is present in the system, for example, the acrylic monomer is present as a co-monomer for the methacrylic monomer.

[0134]

The reaction solution obtained by polymerization contains a mixture of a polymer and a metal complex. Therefore, an organic acid containing a carboxyl group or a sulfonyl group is added to the reaction solution to produce a metal salt with the metal complex so that the metal complex can be removed as a solid by filtration or the like. Then, the impurities such as the acid remaining in the solution are removed by adsorption with basic activated alumina, a basic adsorbent, a solid inorganic acid, an anion exchange resin, or a cellulose anion exchanger to produce a resin solution of the acrylic block copolymer.

[0135]

Then, the polymerization solvent and unreacted monomers remaining in the thus-obtained polymer solution are removed

by evaporation to isolate the acrylic block copolymer. As the evaporation method, a thin-film evaporation method, a flash evaporation method, a horizontal evaporation method using an extrusion screw, or the like can be used. Since the acrylic block copolymer has tackiness, evaporation can be efficiently performed by the horizontal evaporation method using the extrusion screw among these evaporation methods, or by combination of the horizontal evaporation method with another evaporation method.

[0136]

<Process for producing acrylic block copolymer (a)>

A preferred process for producing the acrylic block copolymer (a) comprises heating the acrylic block copolymer (d) at a high temperature of 180°C to 300°C. In this process, the acrylic block copolymer (d) may be heated in the state of the polymer solution under pressure, heated while being subjected to evaporation for removing the solvent from the polymer solution, or directly heat-melted. However, from the viewpoint of reactivity to produce the acid anhydride group and simplicity of production, the copolymer (d) is preferably directly heat-melted. The copolymer (d) is more preferably melt-kneaded.

[0137]

The method of heating the copolymer (d) in the state of the polymer solution can be performed using a pressure-

resistant reactor. The method of heating the copolymer (d) while removing the solvent from the polymer solution by evaporation can be performed by the horizontal evaporation method using the extrusion screw.

[0138]

The method of directly heat-melting the copolymer (d) can be performed using a pressing machine or an injection molding machine.

[0139]

As the method of melt-kneading the copolymer (d), the copolymer (d) may be melt-kneaded by any of various apparatuses capable of heating and kneading at the same time. Examples of such apparatuses include apparatuses ordinarily used for processing rubber, such as a Banbury mixer, a kneader, and a single-screw or multi-screw extruder. As a nonlimiting example, an extruder is preferably used in view of reactivity to the acid anhydride group, and simplicity of production. When the copolymer (d) is melt-kneaded, the melt-kneading time (retention time in an extruder if the extruder is used) may be appropriately determined according to the melt-kneading temperature, the configuration of the screw, L/D (effective length L of the screw/diameter D of the screw), the screw rotational speed, etc.

[0140]

<Method for conversion to carboxylic acid>

The method for producing the carboxyl group (D) in the process for introducing the acid anhydride group (C) into the acrylic block copolymer (a) is not particularly limited, but the copolymer (d) may be heated in the state of the polymer solution under pressure as the introduction method of the acid anhydride group or may be directly heat-melted. From the viewpoint of simplicity of the production, the copolymer (d) is preferably melt-kneaded. When the copolymer (d) is melt-kneaded, the melt-kneading time (retention time in an extruder if the extruder is used) may be appropriately determined according to the melt-kneading temperature, the configuration of the screw, L/D (effective length L of the screw/diameter D of the screw), the screw rotational speed, etc.

[0141]

<Acrylic block copolymer (e)>

When the acrylic block copolymer (a) is required to have higher heat resistance, the carboxyl group (E) may be introduced. A polymer having a carboxyl group has a high glass transition temperature, and for example, polymethacrylic acid has a glass transition temperature of as high as 228°C. Therefore, the heat resistance of the acrylic block copolymer can be further improved by increasing the amount of the constituent monomer of such a polymer. From the viewpoint of cost and simplicity of the

production, the carboxyl group (E) is preferably introduced by a method in which the acid anhydride group of the acrylic block copolymer (a) is hydrolyzed.

[0142]

The reason for this is as follows: In the method for producing the carboxyl group (D) in the process for introducing the acid anhydride group (C) into the acrylic block copolymer (a), the carboxyl group (D) tends to be cyclized with an adjacent ester unit, and when the content of the carboxyl group (D) exceeds 50% by weight, the operation of introducing the carboxyl group (D) tends to become complicated. On the other hand, when a monomer having a carboxyl group is directly introduced by polymerization under polymerization conditions, the monomer having a carboxyl group may deactivate the catalyst used during the polymerization. Japanese Unexamined Patent Application Publication Nos. 2001-234147 and 10-298248 disclose a method for introducing a carboxyl group in which a carboxyl group protected by an appropriate protective group or a functional group which is a precursor of a carboxyl group is introduced into an acrylic block copolymer, and then subjected to selective decomposition. However, this method is disadvantageous in cost and tends to complicate the production.

[0143]

<Carboxyl group (E)>

The carboxyl group (E) is produced by hydrolyzing the acid anhydride group (C), but need not be discriminated from the carboxyl group (D) produced in the process for introducing the acid anhydride group (C). The total content of monomers containing the carboxyl groups (D) and (E) introduced may be 50% by weight or more of the constituent monomers of the acrylic block copolymer (a). The content of the carboxyl groups may be appropriately determined according to the required physical properties of the acrylic block copolymer (a).

[0144]

<Process for producing acrylic block copolymer (e)>

The acrylic block copolymer (e) can be preferably produced by hydrolytic ring-opening of the acid anhydride group (C) of the acrylic block copolymer (a). The method for introducing the carboxyl group (E) by hydrolysis is not particularly limited, and the acrylic block copolymer (a) may be heated together with water under pressure or melt-kneaded together with water. In view of simplicity of the production, the copolymer (a) is preferably melt-kneaded together with water.

[0145]

As the method of heating the acrylic block copolymer (a) together with water under pressure, the copolymer (a)

may be heated in a pressure-resistant reactor. As the method for melt-kneading the acrylic block copolymer (a) together with water, the copolymer (a) may be melt-kneaded by any of various apparatuses capable of heating and kneading at the same time. Examples of such apparatuses include apparatuses ordinarily used for processing rubber, such as a Banbury mixer, a kneader, and a single-screw or multi-screw extruder. In view of reactivity to the acid anhydride group, and simplicity of production, an extruder is preferably used, and a closed extruder is more preferably used. When the acrylic block copolymer (a) is melt-kneaded, the melt-kneading time (retention time in an extruder if the extruder is used) may be appropriately determined according to the melt-kneading temperature, the configuration of the screw, L/D (effective length L of the screw/diameter D of the screw), the screw rotational speed, etc.

[0146]

<Thermoplastic resin composition>

The acrylic block copolymer (a) of the present invention can be used as a composition with the thermoplastic resin (b) and/or the thermoplastic elastomer (c).

[0147]

The acrylic block copolymer (a) is mixed with the thermoplastic resin (b) and/or the thermoplastic elastomer

(c) by the following method: a method of adding the thermoplastic resin (b) or the thermoplastic elastomer (c) to the acrylic block copolymer (a) to improve the physical properties of the acrylic block copolymer (a), such as mechanical properties, hardness, and the like; a method of adding the acrylic block copolymer (a) as a softener to the thermoplastic resin (b) or the thermoplastic elastomer (c) to improve hardness while maintaining the mechanical strength of the thermoplastic resin (b) or the thermoplastic elastomer (c); or a method of adding the acrylic block copolymer (a) as a compatibilizer to at least two types of the thermoplastic resins (b) and/or the thermoplastic elastomers (c) to improve mechanical properties. The mixing ratios of the acrylic block copolymer (a) to the thermoplastic resin (b) and/or the thermoplastic elastomer (c) may be appropriately determined according to demand and are not particularly limited. The composition preferably includes 0.5% by weight to 90% by weight of the acrylic block copolymer (a) and 99.5% by weight to 10% by weight of the thermoplastic resin (b) and/or the thermoplastic elastomer (c).

[0148]

When the thermoplastic resin (b) or the thermoplastic elastomer (c) is added to the acrylic block copolymer (a) to improve physical properties of the acrylic block copolymer

(a), such as mechanical properties, hardness, and the like, the content of the acrylic block copolymer (a) is preferably 90% by weight to 50% by weight, and the content of the thermoplastic resin (b) or the thermoplastic elastomer (c) is preferably 10% by weight to 50% by weight.

[0149]

When the acrylic block copolymer (a) is added as a softener to the thermoplastic resin (b) or the thermoplastic elastomer (c) to improve hardness while maintaining the mechanical strength of the thermoplastic resin (b) or the thermoplastic elastomer (c), the content of the acrylic block copolymer (a) is preferably 0.5% by weight to 50% by weight, and the content of the thermoplastic resin (b) and/or the thermoplastic elastomer (c) is preferably 99.5% by weight to 50% by weight.

[0150]

When the acrylic block copolymer (a) is added as a compatibilizer to at least two types of the thermoplastic resin (b) and/or the thermoplastic elastomer (c) to improve the mechanical properties, the content of the acrylic block copolymer (a) is preferably 0.5% by weight to 20% by weight, and the content the thermoplastic resin (b) and/or the thermoplastic elastomer (c) is preferably 80% by weight to 99.5% by weight.

[0151]

When the content of the acrylic block copolymer (a) is less than 0.5% by weight, the physical properties of the thermoplastic resin (b) and/or the thermoplastic elastomer (c), such as the mechanical properties, hardness, and the like, and compatibility tend not to be sufficiently improved. When the content of thermoplastic resin (b) and/or the thermoplastic elastomer (c) is less than 10% by weight, the physical properties of the acrylic block copolymer (a), such as the mechanical properties, hardness, and the like tend not to be sufficiently improved.

[0152]

<Thermoplastic resin (b)>

Examples of resins usable as the thermoplastic resin (b) in the present invention include, but are not limited to, polyvinyl chloride resins, polyethylene resins, polypropylene resins, cyclic olefin copolymer resins, polymethyl methacrylate resins, styrene-methyl methacrylate resins, acrylonitrile-styrene copolymer resins, polystyrene resins, polyphenylene ether resins, polycarbonate resins, polyester resins, polyamide resins, polyacetal resins, polyphenylene sulfide resins, polysulfone resin, polyimide resins, polyetherimide resins, polyether ketone resins, polyetherether ketone resins, and polyamide-imide resins. These resins may be used alone or in combination of two or more. As a nonlimiting example, a resin having high

compatibility with the acrylic block copolymer (a) is preferably used, and a resin having a functional group reactive with an acid anhydride group is more preferably used. Examples of a functional group reactive with an acid anhydride group include an amino group and a hydroxyl group. Examples of a thermoplastic resin having such a functional group include polyester resins and polyamide resins. Other thermoplastic resins containing a functional group reactive with an acid anhydride can also be preferably used. Polyvinyl chloride resins, polymethyl methacrylate resins, acrylonitrile-styrene copolymer resins, methyl methacrylate-styrene copolymer resins, and polycarbonate resins have high compatibility with the acrylic block copolymer (a). Therefore, the use of such resins has the effect of improving hardness while maintaining mechanical strength, and acting as a compatibilizer with polyester resins and polyamide resins.

[0153]

<Thermoplastic elastomer (c)>

Examples of thermoplastic elastomers usable as the thermoplastic elastomer (c) in the present invention include, but are not limited to, a styrene elastomer, an olefin elastomer, a urethane elastomer, a vinyl chloride elastomer, an ester elastomer, an amide elastomer, and an acrylic elastomer. These may be used alone or in combination or two

or more. Among these elastomers, the acrylic elastomer is preferred from the viewpoint of oil resistance, heat resistance, and compatibility, and the ester elastomer and the amide elastomer are preferred from the viewpoint of oil resistance, heat resistance, and the presence of a functional group reactive to an acid anhydride group. Other thermoplastic elastomers having functional groups reactive to an acid anhydride group can also be preferably used. The use of the styrene elastomer, the olefin elastomer, the urethane elastomer, or the vinyl chloride elastomer has the effect of imparting oil resistance, heat resistance, weather resistance, and flaw resistance, and the like while maintaining elastomer properties, such as rubber elasticity and flexibility.

[0154]

<Process for producing thermoplastic elastomer composition>

As a nonlimiting example of a method for processing or producing the acrylic block copolymer (a) of the present invention or a composition including the acrylic block copolymer (a), the thermoplastic resin (b), and/or the thermoplastic elastomer (c), an existing method including mechanically mixing with, for example, a Banbury mixer, a roller mill, a kneader, a single-screw or multi-screw extruder, or the like, and then pelletizing the resultant mixture can be used. The kneading temperature may be

controlled according to the melting temperatures of the acrylic block copolymer (a), the thermoplastic resin and/or the thermoplastic elastomer (c) used. For example, the kneading temperature for production is preferably 130°C to 300°C.

[0155]

According to demand, another polymer, a stabilizer, a flexibilizer, a lubricant, a flame retardant, a pigment, a filler, a mold release agent, an antistatic agent, an antibacterial-antifungal agent, and the like may be added to the acrylic block copolymer (a) or the composition including the acrylic block copolymer (a), the thermoplastic resin (b), and/or the thermoplastic elastomer (c). As the additives, optimum additives may be appropriately selected according to the required physical properties and purposes of use.

[0156]

Examples of the other polymer include, but are not limited to, styrene-butadiene rubber (SBR), butadiene rubber (BR), isoprene rubber (IR), ethylene-propylene copolymer rubber (EPM), ethylene-propylene-diene copolymer rubber (EPDM), acrylonitrile-butadiene copolymer rubber (NBR), chloroprene rubber, butyl rubber (IIR), urethane rubber, silicone rubber, polysulfide rubber, hydrogenated nitrile rubber, fluororubber, tetrafluoroethylene-propylene rubber, tetrafluoroethylene-propylene-vinylidene fluoride rubber,

acrylic rubber (ACM), chlorosulfonated polyethylene rubber, epichlorohydrin rubber (CO), ethylene-acrylic rubber, and norbornene rubber. These may be used alone or in combination of two or more.

[0157]

Examples of the stabilizer include, but are not limited to, compounds, such as triphenylphosphite, hindered phenol, dibutyltin maleate. These compounds may be used alone or in combination of two or more.

[0158]

Examples of the flexibilizer include, but are not limited to, compounds, such as plasticizers ordinarily added to thermoplastic resins and rubber; softeners such as process oil; oligomers; oils, such as animal oil and vegetable oil; petroleum fractions, such as kerosene, light oil, heavy oil, and naphtha. Examples of the softeners include process oils, for example, petroleum process oils, such as paraffin oil, naphthenic process oil, aromatic process oil. Examples of the plasticizers include phthalic acid derivatives, such as dimethyl phthalate, diethyl phthalate, di-n-butyl phthalate, di-(2-ethylhexyl) phthalate, diheptyl phthalate, diisodecyl phthalate, di-n-octyl phthalate, diisononyl phthalate, ditridecyl phthalate, octyldecyl phthalate, butylbenzyl phthalate, and dicyclohexyl phthalate; isophthalic acid derivatives, such

as dimethyl isophthalate; tetrahydrophthalic acid derivatives, such as di-(2-ethylhexyl)tetrahydrophthalic acid; adipic acid derivatives, such as dimethyl adipate, dibutyl adipate, di-n-hexyl adipate, di-(2-ethylhexyl) adipate, isononyl adipate, diisodecyl adipate, and dibutyl diglycol adipate; azelaic acid derivatives, such as di-2-ethylhexyl azelate; sebacic acid derivatives, such as dibutyl sebacate; dodecan-2-oic acid derivatives; maleic acid derivatives, such as dibutyl maleate and di-2-ethylhexyl maleate; fumaric acid derivatives, such as dibutyl fumarate; p-oxybenzoic acid derivatives, such as 2-ethylhexyl p-oxybenzoate; trimellitic acid derivatives, such as tris-2-ethylhexyl trimellitate; pyromellitic acid derivatives; citric acid derivatives, such as acetyl tributyl citrate; itaconic acid derivatives; oleic acid derivatives; ricinoleic acid derivatives; stearic acid derivatives; other fatty acid derivatives; sulfonic acid derivatives; phosphoric acid derivatives; glutaric acid derivatives; polyester plasticizers comprising a polymer of a dibasic acid such as adipic acid, azelaic acid, phthalic acid, or the like, and a glycol or a monohydric alcohol; glycol derivatives; glycerin derivatives; paraffin derivatives, such as chlorinated paraffin; epoxy derivatives; polyester polymer plasticizers; polyether polymer plasticizers; carbonate derivatives, such as

ethylene carbonate and propylene carbonate; benzenesulfonic acid derivatives, such as N-butylbenzenesulfonamide. In the present invention, the plasticizer is not limited to these plasticizers, and various plasticizers can be used. Also, commercially available plasticizers for rubber or thermoplastic resins can be used. Examples of the commercially available plasticizers include Thiokol TP (produced by Morton Corporation), Adekacizer O-130P, C-79, UL-100, P-200, and RS-735 (produced by Asahi Denka Co., Ltd.), Sansocizer N-400 (produced by Shin-Nippon Rika Co., Ltd.), BM-4 (produced by Daihachi Chemical Industry Ltd.), and EHPB (produced by Ueno Fine Chemicals Industry, Ltd.). Examples of vegetable oil include castor oil, cottonseed oil, linseed oil, rapeseed oil, soybean oil, palm oil, coconut oil, peanut oil, pine oil, and tall oil.

[0159]

The flexibilizer used preferably has excellent affinity for the acrylic block copolymer (a), the thermoplastic resin (b), and the thermoplastic elastomer (c). Preferred examples of such a flexibilizer include, but are not limited to, low-volatile plasticizers causing small heating losses, such as adipic acid derivatives, phthalic acid derivatives, glutaric acid derivatives, trimellitic acid derivatives, pyromellitic acid derivatives, polyester plasticizers, glycerin derivatives, epoxy derivatives; polyester polymer

plasticizers, and polyether polymer plasticizers. These flexibilizers may be used alone or in combination of two or more.

[0160]

Examples of the lubricant include, but are not limited to, compounds, such as polyethylene wax, polypropylene wax, and montan wax. These compounds may be used alone or in combination of two or more.

[0161]

Examples of the flame retardant include, but are not limited to, compounds, such as triphenyl phosphate, tricresyl phosphate, decabromobiphenyl, decabromobiphenyl ether, and antimony trioxide. These compounds may be used alone or in combination of two or more.

[0162]

Examples of the pigment include, but are not limited to, compounds, such as titanium oxide, zinc sulfide, and zinc oxide. These compounds may be used alone or in combination of two or more.

[0163]

Examples of the filler include, but are not limited to, compounds, such as carbon black, glass fibers, metal fibers, potassium titanate whiskers, asbestos, wollastonite, mica, talc, calcium carbonate, glass flakes, milled fibers, and metal powders. These compounds may be used alone or in

combination of two or more.

[0164]

<Automobile, electric, and electronic parts>

The acrylic block copolymer (a) of the present invention and the composition comprising the acrylic block copolymer (a), the thermoplastic resin (b), and/or the thermoplastic elastomer (c) are improved in oil resistance, heat resistance, mechanical properties, etc. while maintaining the characteristics inherent to acrylic block copolymers. Therefore, the acrylic block copolymer (a) and the composition can be more preferably used for automobile, electric and electronic parts. Specific examples of such parts include various types of oil seals, such as an oil seal and a reciprocation oil seal; various types of packings, such as a ground packing, a lip packing, and a squeeze packing; various types of boots, such as a constant velocity joint boot, a strut boot, a rack and pinion boot, a brake booster boot, and a steering ball joint boot; various types of dust covers, such as a suspension dust cover, a suspension tie-rod dust cover, and a stabilizer tie-rod dust cover; various types of gaskets, such as a resin intake manifold gasket, a throttle-body gasket, a power-steering vane pump gasket, a head-cover gasket, a water heater self-priming pump gasket, a filter gasket, a pipe joint (ABS & HBB) gasket, a HDD top-cover gasket, a HDD connector gasket,

a cylinder-head gasket combined with a metal, a car cooler compressor gasket, a gasket around an engine, an AT separate plate, and general-purpose gaskets (industrial sewing machine, nailing machine, and the like); various types of valves, such as a needle valve, a plunger valve, a water/gas valve, a brake valve, a drinking valve, and a safety valve for an aluminum electrolytic capacitor; various types of stopper mainly having a buffer function, such as a diaphragm for a vacuum booster or water and gas, a seal washer, a bore plug, and a high-precision stopper; and precision seal rubbers, such as a plug tube seal, an injection pipe seal, an oil receiver, a brake drum seal, a shading seal, a plug seal, a connector seal, and a keyless entry cover.

[0165]

The above-described products can be molded by any desired molding method such as extrusion molding, compression molding, blow molding, calender molding, vacuum molding, foam molding, injection molding, powder slash molding, injection blowing, or the like using the polymer or the composition thereof.

In addition to the automobile, electric and electronic parts, the acrylic block copolymer (a) and the composition comprising the acrylic block copolymer (a), the thermoplastic resin (b), and/or the thermoplastic elastomer (c) can be preferably widely used for a hose, a sheet, a

film material, a damping material, a base polymer of an adhesive, a resin modifier, and the like in the fields of package materials, construction and civil engineering, miscellaneous goods, and the like.

[0166]

[Examples]

Although the present invention will be described in detail below on the basis of examples, the present invention is not limited to these examples.

[0167]

In the examples, BA, EA, MEA, MMA, TBMA, and TBA represent butyl acrylate, ethyl acrylate, methoxyethyl acrylate, methyl methacrylate, tert-butyl methacrylate, and tert-butyl acrylate, respectively.

[0168]

<Test method>

(Molecular weight)

In each of the examples, a molecular weight was determined in terms of polystyrene by GPC measurement using a GPC analyzer, chloroform as a mobile phase, and a polystyrene gel column. The GPC measurement was performed using the GPC analyzer (system: GPC system produced by Waters Corporation, column: Shodex K-804 (polystyrene gel) produced by Showa Denko K.K.) and chloroform as the mobile phase. The molecular weight was determined in terms of

polystyrene.

[0169]

(Analysis of conversion to acid anhydride group)

Reaction of conversion to an acid anhydride group in an acrylic block copolymer was confirmed by an infrared spectrum (FTIR-8100 produced by Shimadzu Corporation) and nuclear magnetic resonance (AM400 produced by BRUKER Corporation).

[0170]

As a measurement solvent for nuclear magnetic resonance analysis, deuteriochloroform was used for both a block having a carboxylic ester and a block having an acid anhydride structure.

[0171]

(Analysis of conversion to acid)

Reaction of carboxylic acid decomposition in an acrylic block copolymer was confirmed by an infrared spectrum (FTIR-8100 produced by Shimadzu Corporation) and nuclear magnetic resonance (AM400 produced by BRUKER Corporation).

[0172]

As a measurement solvent for nuclear magnetic resonance analysis, deuteriochloroform was used for a block having a carboxylic ester, and deuteromethanol was used for a block containing a carboxylic acid.

[0173]

(Hardness)

Hardness at 23°C (JIS A or JIS D) was measured according to JIS K6301.

[0174]

(Mechanical strength)

According to the method of JIS K7113, mechanical strength was measured by AG-10TB model autograph produced by Shimadzu Corporation. Measurement was performed with $n = 3$, and averages of strength (MPa) and elongation (%) at breakage of a specimen were used. The specimen had a shape of No. 2(1/3) having a thickness of about 2 mm. A test was carried out at 23°C and a test rate of 500 mm/min. As a rule, the specimen was conditioned at a temperature of $23 \pm 2^\circ\text{C}$ and relative humidity of $50 \pm 5\%$ for 48 hours or more before the test.

[0175]

(Compression set)

According to JIS K6301, a cylindrical molded product was maintained with a compression rate of 25% at 70°C or 100°C for 22 hours, and then allowed to stand at room temperature for 30 minutes. Then, the thickness of the molded product was measured to calculate residual strain. Namely, a compression set of 0% corresponds to complete recovery of strain, and a compression set of 100% corresponds to no recovery of strain.

[0176]

(Oil resistance)

According to ASTM D638, a molded product of a composition was maintained in ASTM No. 3 oil kept at 150°C for 72 hours to determine a rate of weight change (% by weight).

[0177]

(Heat resistance)

Heat resistance was evaluated by comparison of flow beginning temperatures. A flow beginning temperature was measured by extruding a resin from a nozzle having an inner diameter of 1 mm and a length of 10 mm under a load of 60 Kg/cm² while heating the resin at a heating rate of 5°C/min using a Kokashiki flow tester CFT-500C model produced by Shimadzu Corporation. The temperature at start of lowering of a resin extrusion piston of the flow tester (indicated by Tfb in the measuring meter) was regarded as the flow beginning temperature.

[0178]

(Thermogravimetry)

The thermal decomposition resistance of an acrylic block copolymer was measured with a thermal and differential thermogravimetric analyzer (DTG-50) produced by Shimadzu Corporation. Measurement was performed under a nitrogen stream at a flow rate of 50.0 ml/min and a heating rate of

10.0°C/min. The 5% weight loss temperature was determined on the basis of the weight at 100°C.

[0179]

(Insoluble matter ratio (% by weight))

In order to measure an insoluble matter ratio, 1 g (Wu) of a sample was covered with a 100-mesh wire gauze and immersed in toluene at 60°C for 24 hours, and a toluene soluble matter was separated. Then, the residual solid was dried under vacuum at 60°C, and the weight g (Wc) of the residual solid after drying was measured. The insoluble matter ratio was determined from the weight of the residual solid (Wc) relative to 1 g (Wu) of the sample. The progress of reaction can be confirmed by the insoluble matter ratio (% by weight).

[0180]

<Production of acrylic block copolymer>

Production Example 1

Synthesis of (MMA-co-TBMA)-b-BA-b-(MMA-co-TBMA) (MMA/TBMA = 50/50 mol%, BA/(MMA-co-TBMA) = 70/30% by weight) acrylic block copolymer (referred to as "50TBA7" hereinafter)

The procedures below were preformed for producing 50TBA7. The air in a 5-L separable flask used as a polymerization vessel was replaced by nitrogen, and 11.3 g (78.5 mmol) of copper bromide and 180 mL of acetonitrile (bubbled with nitrogen) were added to the flask. After

stirring under heating at 70°C for 30 minutes, 5.65 g (15.7 mmol) of diethyl 2,5-dibromoadipate serving as an initiator and 900 ml (6.28 mol) of BA were added to the flask. The resultant mixture was stirred under heating at 85°C, and 1.64 ml (7.85 mmol) of diethylenetriamine was added as a ligand to initiate polymerization.

[0181]

After the initiation of polymerization, 0.2 mL of a solution was sampled from the polymerization solution with predetermined time intervals, and the BA conversion rate was determined by gas chromatographic analysis of the sampled solution. The polymerization rate was controlled by adding triamine at any desired time. At a BA conversion rate of 95%, 351 ml (2.16 mol) of TBMA, 232 ml (2.16 mol) of MMA, 7.77 g (78.5 mmol) of copper chloride, 1.64 ml (7.85 mmol) of diethylenetriamine, and 1148 ml of toluene (bubbled with nitrogen) were added to the reaction solution. Similarly, the conversion rates of TBMA and MMA were determined. At a TBMA conversion rate of 70% and an MMA conversion rate of 62%, 1500 ml of toluene was added to the reaction solution, and the reactor was cooled in a water bath to terminate the reaction.

[0182]

The reaction solution was diluted with 2.0 L of toluene, and then 17.9 g of p-toluenesulfonic acid monohydrate was

added to the reaction solution, followed by stirring at room temperature for 3 hours. Then, 12.0 g of Kyowaad 500SH (produced by Kyowa Chemical Industry Co., Ltd.) was added as an adsorbent to the polymer solution, followed by further stirring at room temperature for 3 hours. Then, the adsorbent was filtered off with a Kiriya funnel to produce a colorless transparent polymer solution. The resultant solution was dried to remove the solvent and the residual monomers, and thereby the target acrylic block copolymer 50TBA7 was obtained.

[0183]

GPC analysis of the resultant acrylic block copolymer 50TBA7 showed a number-average molecular weight M_n of 108,240 and a molecular weight distribution M_w/M_n of 1.49.

[0184]

Production Example 2

Synthesis of (MMA-co-TBMA)-b-BA-b-(MMA-co-TBMA) (MMA/TBMA = 80/20 mol%, BA/(MMA-co-TBMA) = 70/30% by weight) acrylic block copolymer (referred to as "20TBA7" hereinafter)

The target acrylic block copolymer 20TBA7 was produced by the same method as in Production Example 1 except the following procedures: In a 5-L separable flask, 5.65 g (15.7 mmol) of diethyl 2,5-dibromoadipate and 900 ml (6.28 mol) of BA were charged and subjected to polymerization. At a BA conversion rate of 95%, 151.9 ml (0.94 mol) of TBMA and

400.9 ml (3.77 mol) of MMA were added to the reaction solution. At a TBMA conversion rate of 70% and an MMA conversion rate of 64%, the reaction was terminated.

[0185]

GPC analysis of the resultant acrylic block copolymer 20TBA7 showed a number-average molecular weight M_n of 122,858 and a molecular weight distribution M_w/M_n of 1.46.

[0186]

Production Example 3

Synthesis of (MMA-co-TBMA)-b-(BA-co-EA-co-MEA)-b-(MMA-co-TBMA) (MMA/TBMA = 80/20 mol%, (BA-co-EA-co-MEA)/(MMA-co-TBMA) = 70/30% by weight) acrylic block copolymer (referred to as "20T3A7" hereinafter)

The target acrylic block copolymer 20T3A7 was produced by the same method as in Production Example 1 except the following procedures: In a 5-L separable flask, 5.89 g (16.4 mmol) of diethyl 2,5-dibromoadipate, 362 ml (2.52 mol) of BA, 344 ml (3.17 mol) of EA, and 195 ml (1.51 mol) of MEA were charged and subjected to polymerization. At a BA conversion rate of 95%, an EA conversion rate of 95%, and an MEA conversion rate of 97%, 158 ml (0.98 mol) of TBMA and 418 ml (3.92 mol) of MMA were added to the reaction solution. At a TBMA conversion rate of 64% and an MMA conversion rate of 59%, the reaction was terminated.

[0187]

GPC analysis of the resultant acrylic block copolymer 20T3A7 showed a number-average molecular weight M_n of 111,000 and a molecular weight distribution M_w/M_n of 1.47.

[0188]

Production Example 4

Synthesis of (MMA-co-TBMA)-b-(BA-co-EA-co-MEA)-b-(MMA-co-TBMA) (MMA/TBMA = 80/20 mol%, (BA-co-EA-co-MEA)/(MMA-co-TBMA) = 60/40% by weight) acrylic block copolymer (referred to as "20T3A6" hereinafter)

The target acrylic block copolymer 20T3A6 was produced by the same method as in Production Example 1 except the following procedures: In a 5-L separable flask, 5.31 g (14.8 mmol) of diethyl 2,5-dibromoadipate, 281 ml (1.96 mol) of BA, 267 ml (2.47 mol) of EA, and 151 ml (1.18 mol) of MEA were charged and subjected to polymerization. At a BA conversion rate of 95%, an EA conversion rate of 95%, and an MEA conversion rate of 97%, 193 ml (1.20 mol) of TBMA and 509 ml (4.78 mol) of MMA were added to the reaction solution. At a TBMA conversion rate of 64% and an MMA conversion rate of 61%, the reaction was terminated.

[0189]

GPC analysis of the resultant acrylic block copolymer 20T3A6 showed a number-average molecular weight M_n of 118,927 and a molecular weight distribution M_w/M_n of 1.49.

[0190]

Production Example 5

Synthesis of (MMA-co-TBMA)-b-(BA-co-EA-co-MEA)-b-(MMA-co-TBMA) (MMA/TBMA = 50/50 mol%, (BA-co-EA-co-MEA)/(MMA-co-TBMA) = 60/40% by weight) acrylic block copolymer (referred to as "50T3A6" hereinafter)

The target acrylic block copolymer 50T3A6 was produced by the same method as in Production Example 1 except the following procedures: In a 5L separable flask, 5.31 g (14.8 mmol) of diethyl 2,5-dibromoadipate, 281 ml (1.96 mol) of BA, 267 ml (2.47 mol) of EA, and 151 ml (1.18 mol) of MEA were charged and subjected to polymerization. At a BA conversion rate of 95%, an EA conversion rate of 95%, and an MEA conversion rate of 98%, 435 ml (2.70 mol) of TBMA and 287 ml (2.70 mol) of MMA were added to the reaction solution. At a TBMA conversion rate of 67% and an MMA conversion rate of 59%, the reaction was terminated.

[0191]

GPC analysis of the resultant acrylic block copolymer 50T3A6 showed a number-average molecular weight M_n of 96,778 and a molecular weight distribution M_w/M_n of 1.46.

[0192]

Production Example 6

Synthesis of TBMA-b-(BA-co-EA-co-MEA)-b-TBMA ((BA-co-EA-co-MEA)/TBMA = 60/40% by weight) acrylic block copolymer (referred to as "100T3A6" hereinafter)

The target acrylic block copolymer 100T3A6 was produced by the same method as in Production Example 1 except the following procedures: In a 5L separable flask, 5.69 g (15.8 mmol) of diethyl 2,5-dibromoadipate, 301 ml (2.10 mol) of BA, 286 ml (2.64 mol) of EA, and 162 ml (1.26 mol) of MEA were charged and subjected to polymerization. At a BA conversion rate of 96%, an EA conversion rate of 96%, and an MEA conversion rate of 98%, 636 ml (3.94 mol) of TBMA was added to the reaction solution. At a TBMA conversion rate of 77%, the reaction was terminated.

[0193]

GPC analysis of the resultant acrylic block copolymer 100T3A6 showed a number-average molecular weight M_n of 90,416 and a molecular weight distribution M_w/M_n of 1.43.

[0194]

Production Example 7

Synthesis of MMA-b-(BA-co-TBA)-b-MMA (BA/TBA = 97.5/2.5 mol%, (BA-co-TBA)/MMA = 70/30% by weight) acrylic block copolymer (referred to as "2.5STBA7" hereinafter)

The target acrylic block copolymer 2.5STBA7 was produced by the same method as in Production Example 1 except the following procedures: In a 5L separable flask, 5.65 g (15.7 mmol) of diethyl 2,5-dibromoadipate, 877 ml (6.12 mol) of BA, and 22.9 ml (0.16 mol) of TBA were charged and subjected to polymerization. At a BA conversion rate of

95% and a TBA conversion rate of 95%, 369 ml (3.45 mol) of MMA was added to the reaction mixture. At an MMA conversion rate of 65%, the reaction was terminated.

[0195]

GPC analysis of the resultant acrylic block copolymer 2.5STBA7 showed a number-average molecular weight M_n of 116,000 and a molecular weight distribution M_w/M_n of 1.52.

[0196]

Production Example 8

Synthesis of MMA-BA-MMA (BA/MMA = 70/30% by weight) acrylic block copolymer (referred to as "MBAM" hereinafter)

The procedures below were performed for producing MBAM.

[0197]

The air in a 5L separable flask used as a polymerization vessel was replaced by nitrogen, and 11.3 g (78.5 mmol) of copper bromide and 180 ml of acetonitrile (dried over molecular sieves and then bubbled with nitrogen) were added to the flask. After stirring under heating at 70°C for 5 minutes, the temperature was returned to room temperature, and then 5.7 g (15.7 mmol) of diethyl 2,5-dibromoadipate serving as an initiator and 804.6 g (900.0 ml) of n-butyl acrylate were added to the flask. The resultant mixture was stirred under heating at 80°C, and 1.6 ml (7.9 mmol) of diethylenetriamine was added as a ligand to initiate polymerization. After the initiation of

polymerization, about 0.2 mL of a solution was sampled from the polymerization solution with predetermined time intervals, and the conversion rate of butyl acrylate was determined by gas chromatographic analysis of each sampled solution. The polymerization rate was controlled by adding triamine at any desired time. At a conversion rate of n-butyl acrylate of 95%, 345.7 g (369.3 ml) of methyl methacrylate, 7.8 g (78.5 mmol) of copper chloride, 1.6 ml (7.9 mmol) of diethylenetriamine, and 1107.9 ml of toluene (dried over molecular sieves and then bubbled with nitrogen) were added to the reaction solution. Similarly, the conversion rate of methyl methacrylate was determined. At a conversion rate of methyl methacrylate of 85% and a conversion rate of n-butyl acrylate of 98%, 1500 ml of toluene was added to the reaction solution, and the reactor was cooled in a water bath to terminate the reaction. The polymerization solution was constantly green during the reaction.

[0198]

The reaction solution was diluted with 4000 ml of toluene, and then 22.1 g of p-toluenesulfonic acid monohydrate was added to the reaction solution, followed by stirring at room temperature for 3 hours. The insoluble precipitate was filtered off with a Kiriya funnel, and then 9.7 g of Kyowaad 500SH was added as an adsorbent to the

resultant polymer solution, followed by further stirring at room temperature for 3 hours. Then, the adsorbent was filtered off with a Kiriya funnel to produce a colorless transparent polymer solution. The resultant solution was dried to remove the solvent and the residual monomers, and thereby the target acrylic block copolymer MBAM was obtained.

[0199]

GPC analysis of the resultant acrylic block copolymer MBAM showed a number-average molecular weight M_n of 119,200 and a molecular weight distribution M_w/M_n of 1.51. Also, NMR analysis of the composition showed that BA/MMA = 72/28 (% by weight).

[0200]

Production Example 9

Synthesis of MMA-b-(BA-co-EA-co-MEA)-b-MMA ((BA-co-EA-co-MEA)/MMA = 70/30% by weight) acrylic block copolymer (referred to as "M3AM" hereinafter)

The procedures below were performed for producing M3AM.

[0201]

The air in a 500ml separable flask used as a polymerization vessel was replaced by nitrogen, and 1.37 g (9.5 mmol) of copper bromide, 20 mL of acetonitrile (bubbled with nitrogen), 0.69 g (1.9 mmol) of diethyl 2,5-dibromoadipate serving as an initiator, 40.2 ml (280 mmol), 38.2 ml (352 mmol) of EA, and 21.6 ml (168 mmol) of MEA were

added to the flask by the same procedures as in Example 1. Then, 0.20 ml (1.0 mmol) of diethylenetriamine was added as a ligand to initiate polymerization.

[0202]

At a BA conversion rate of 95%, an EA conversion rate of 95%, and an MEA conversion rate of 96%, 42.8 ml (400 mmol) of MMA, 1.82 g (18.5 mmol) of copper chloride, 0.20 ml (1.0 mmol) of diethylenetriamine, and 128.5 ml of toluene (bubbled with nitrogen) were added to the reaction solution. At a BA conversion rate of 97%, an EA conversion rate of 97%, and an MEA conversion rate of 98%, and an MMA conversion rate of 82%, 150 ml of toluene was added to the reaction solution, and the reactor was cooled in a water bath to terminate the reaction.

[0203]

The reaction solution was diluted with 400 ml of toluene, and then 2.21 g of p-toluenesulfonic acid monohydrate was added to the reaction solution, followed by stirring at room temperature for 3 hours. The insoluble precipitate was filtered off with a Kiriyaama funnel, and then 0.97 g of Kyowaad 500SH was added as an adsorbent to the resultant polymer solution, followed by further stirring at room temperature for 3 hours. Then, the adsorbent was filtered off with a Kiriyaama funnel to produce a colorless transparent polymer solution. The resultant solution was

dried to remove the solvent and the residual monomers, and thereby the target acrylic block copolymer M3AM was obtained.

[0204]

GPC analysis of the resultant acrylic block copolymer showed a number-average molecular weight M_n of 113,000 and a molecular weight distribution M_w/M_n of 1.49. Also, NMR analysis of the composition showed that EA/BA/MEA/MMA = 24/33/15/28 (% by weight).

[0205]

Example 1

Reaction of conversion to acid anhydride group in acrylic block copolymer 50TBA7 and characteristic evaluation

First, 45 g of the acrylic block copolymer 50TBA7 produced in Production Example 1 and 0.09 g of Irganox 1010 (produced by Ciba Specialty Chemicals Inc.) were melt-kneaded at 100 rpm for 20 minutes with Labo Plastomill (produced by Toyo Seiki Co., Ltd.) set to 240°C to produce the target acid anhydride group-containing acrylic block copolymer (referred to as "50ANBA7" hereinafter).

Conversion to an acid anhydride group of a tert-butyl ester site could be confirmed by IR (infrared absorption spectrum) and ^{13}C -NMR (nuclear magnetic resonance spectrum). Namely, in IR, an absorption spectrum derived from the acid anhydride group was observed at about 1800 cm^{-1} after conversion. In ^{13}C -NMR, signals at 82 ppm derived from

methine carbon and 28 ppm derived from methyl carbon of a tert-butyl group, respectively, disappeared after conversion. The resultant bulk sample was molded by heat pressing at 240°C to produce a cylindrical molded product of 30 mm in diameter and 12 mm in thickness for evaluating compression set. The molded product was used for measuring hardness and compression set. Similarly, a molded sheet product having a thickness of 2 mm was produced by heat pressing. The molded sheet product was used for measuring oil resistance, mechanical strength, and heat resistance.

[0206]

Thermogravimetry of the acid anhydride group-containing acrylic block copolymer 50ANBA7 showed a 5% weight loss temperature of 357°C.

[0207]

Examples 2 to 7

Reaction of conversion to acid anhydride group and characteristic evaluation

The acrylic block copolymers produced in Production Examples 2 to 7 were used for producing acid anhydride group-containing acrylic block copolymers (the resultant acrylic block copolymers are referred to as "20ANBA7", "20AN3A7", "100AN3A6", "50AN3A6", and "20AN3A6", respectively, hereinafter) according to the same procedures as in Example 1. Also, cylindrical molded products of 30 mm

in diameter and 12 mm in thickness for evaluating compression set were formed by the same procedures as in Example 1. These molded products were used for measuring hardness and compression set. Similarly, molded sheet products of 2 mm in thickness were formed by heat pressing. These sheet products were used for measuring oil resistance, mechanical strength, and heat resistance.

[0208]

Comparative Examples 1 and 2

First, 100 parts by weight of each the copolymers produced in Production Examples 8 and 9 was mixed with 0.2 parts by weight of Irganox 1010 (Ciba Specialty Chemicals Inc.), and the resultant mixture was melt-kneaded at 50 rpm for 20 minutes with Labo Plastomill (produced by Toyo Seiki Co., Ltd.) set at 190°C to produce a bulk sample. The resulting samples were heat-pressed at 190°C to obtain cylindrical molded products of 30 mm in diameter and 12 mm in thickness for evaluating compression set. These molded products were used for measuring hardness and compression set. Similarly, molded sheet products of 2 mm in thickness were formed by heat pressing. These sheet products were used for measuring oil resistance, mechanical strength, and heat resistance. As a result of thermogravimetry of the acrylic block copolymer MBAM not containing an acid anhydride group and produced in Comparative Example 1, the

5% weight loss temperature was 280°C.

[0209]

Comparative Example 3

Santoprene 211-55 (AES Japan Co., Ltd.), which was an olefinic elastomer, was melt-kneaded with Labo Plastomill (produced by Toyo Seiki Co., Ltd.) set at 170°C at a screw rotational speed of 100 rpm to obtain a sample. The resulting sample was heat-pressed at 170°C to obtain a cylindrical molded product of 30 mm in diameter and 12 mm in thickness. The molded product was used for measuring hardness and compression set. Similarly, a molded sheet product of 2 mm in thickness was formed by heat pressing at 170°C. The sheet product was used for measuring oil resistance, mechanical strength, and heat resistance. As a result, it was found that with the olefinic elastomer, the compression set was good, but the oil resistance was at an insufficient level.

[0210]

Comparative Example 4

Pelprene P-30B (Toyobo Co., Ltd.), which was an ester elastomer, was melt-kneaded with Labo Plastomill (produced by Toyo Seiki Co., Ltd.) set at 190°C at a screw rotational speed of 50 rpm to obtain a sample. The resulting sample was heat-pressed at 190°C to obtain a cylindrical molded product of 30 mm in diameter and 12 mm in thickness. The

molded product was used for measuring hardness and compression set. Similarly, a molded sheet product of 2 mm in thickness was formed by heat pressing at 190°C. The sheet product was used for measuring oil resistance, mechanical strength, and heat resistance. As a result, it was found that with the polyester elastomer, excellent mechanical properties are exhibited, but flexibility is unsatisfactory even at a low-hardness grade, and the oil resistance and compression set are also unsatisfactory.

[0211]

[Table 1]

Table 1

	Example							Comparative Example			
	1	2	3	4	5	6		1	2	3	4
Polymer	50ANBA7	20ANBA7	20AN3A7	100AN3A6	50AN3A6	20AN3A6		MBAM	M3AM	211-55	P-30B
Hardness JIS-A	9	14	36	23	-	45		22	38	53	79
Breaking strength (MPa)	6.5	6.4	6.9	5.5	8.7	11.2		8.6	6.6	4.5	25
Breaking elongation (%)	369	354	531	372	320	295		339	621	438	1426
Heat resistance (°C)	126	-	125	148	157.4	-		119	111	154.3	144.5
Oil resistance (wt%)	57.3	-	19.9	20.6	-	-		54.9	21	189.5	64
Compression set (%)	42	32	51		-			49	76	28.7	65
				39.5		57					
5% weight loss temp.(°C)	357	-	-	-	-	-		280	-	-	-

[0212]

Table 1 (Examples 1 to 7 and Comparative Examples 1 to 4) indicates that the thermoplastic elastomer compositions of the present invention have excellent compression set, oil resistance, and heat resistance, and maintains strength required for molding or the like. It is also found that the cohesive force is improved by introducing a functional group, but the compositions are materials exhibiting low hardness, flexibility, and excellent compression set and mechanical strength.

[0213]

Example 8

Reaction of conversion to acid anhydride group in 20T3A6

First, 100 parts by weight of the polymer 20T3A6 produced in Production Example 4 was mixed with 0.2 parts by weight of Irganox 1010 (Ciba Specialty Chemicals Inc.), and the resultant mixture was kneaded and extruded with a vented twin screw extruder (44 mm, L/D = 42.25) (produced by Japan Steel Works, Ltd.) at a rotational speed of 50 rpm and at 240°C to produce the target acid anhydride group-containing acrylic block copolymer (20AN3A6). As in Example 1, conversion to an acid anhydride group of a tert-butyl ester site could be confirmed by IR (infrared absorption spectrum) and ¹³C-NMR (nuclear magnetic resonance spectrum). It was thus confirmed that an acid anhydride group-containing

acrylic block copolymer can be produced by any of various processing machines, and that such a block copolymer can be produced by an extruder to simplify the production process.

[0214]

<Thermal decomposition resistance of acid anhydride group-containing block>

As a result of thermogravimetric analysis of the acid anhydride group-containing acrylic block copolymer 50ANBA7, the 5% weight loss temperature was 357°C.

[0215]

As a result of thermogravimetry of the acid anhydride group-containing acrylic block copolymer MBAM not containing an acid anhydride group, the 5% weight loss temperature was 280°C.

[0216]

These results indicate that the introduction of an acid anhydride group has the effect of significantly improving thermal decomposition resistance.

[0217]

<Thermoplastic resin composition>

Example 9

First, 100 parts by weight of polybutylene terephthalate resin (Duranex 2002 produced by Polyplastics Co., Ltd.) was added to 100 parts by weight of 20ANBA7, and the resultant mixture was kneaded for 20 minutes by Labo

Plastomill set at 240°C at a rotational speed of 100 rpm to obtain a bulk sample. The resultant bulk sample was heat-pressed at 240°C to obtain a molded product of 2 mm in thickness for evaluating physical properties.

Test samples with predetermined shapes were punched from the molded product and used for evaluating the physical properties.

[0218]

Example 10

A molded product for evaluation was formed by the same method as in Example 9 except that 100 parts by weight of Daiamid E47-S1 (Daicel Huls Ltd.) was added to 100 parts by weight of the acid anhydride group-containing acrylic block copolymer 20ANBA7, and the resultant mixture was kneaded for 20 minutes with Labo Plastomill set at 190°C at a rotational speed of 100 rpm, and then heat-pressed at 190°C.

[0219]

Example 11

A molded product for evaluation was formed by the same method as in Example 9 except that 100 parts by weight of Ubesta 3012U (Ube Industries, Ltd.) was added to 100 parts by weight of 20ANBA7.

[0220]

Comparative Example 6

First, polybutylene terephthalate resin (Duranex 2002

produced by Polyplastics Co., Ltd.) was kneaded for 20 minutes with Labo Plastomill set at 240°C at a rotational speed of 100 rpm to obtain a bulk sample. The resultant bulk sample was heat-pressed at 240°C to obtain a molded product of 2 mm in thickness for evaluating physical properties.

[0221]

Test samples with predetermined shapes were punched from the molded product and used for evaluating the physical properties.

[0222]

Comparative Example 7

A molded product for evaluation was formed by the same method as in Comparative Example 6 except that Daiamid E47-S1 (Daicel Huls Ltd.) was used.

[0223]

Comparative Example 8

A molded product for evaluation was formed by the same method as in Comparative Example 6 except that Ubesta 3012U (Ube Industries, Ltd.) was used.

[0224]

Comparative Example 9

A molded product for evaluation was formed by the same method as in Comparative Example 6 except that 20ANBA7 was used.

[0225]

[Table 2]

Table 2

	Example			Comparative Example				
	9	10	11	6	7	8	9	
Polymer	20ANBA7	20ANBA7	20ANBA7	-	-	-	20ANBA7	
Thermoplastic resin	2002	-	3012U	2002	-	3012U	-	
Thermoplastic elastomer	-	E47-S1	-	-	E47-S1	-	-	
Hardness JIS-A	74	61	79	-	-	-	14	
Hardness JIS-D	-	-	-	83	52	84	-	
Insoluble substances(wt%)	-	79.8	83.4	100	100	100	0	

[0226]

Table 2 (Examples 9 to 11 and Comparative Examples 6 to 9) indicates that according to the present invention, a molded product having desired flexibility can be obtained. In Examples 10 and 11, measurement of acetone-insoluble substances shows reaction between the resin and the acid anhydride group-containing block copolymer. Furthermore, the compositions can be preferably used as compatibilizers.

[0227]

<Compatibilizer>

Example 12

First, 25 parts by weight of Ubesta 3012U (Ube Industries, Ltd.) and 4 parts by weight of 20ANBA7 were added to 100 parts by weight of MBAM, and the resultant mixture was kneaded for 20 minutes with Labo Plastomill set at 240°C at a rotational speed of 100 rpm to obtain a bulk sample. The resultant sample was heat-pressed at 240°C to obtain a molded product of 2 mm in thickness for evaluating physical properties.

[0228]

A test piece with a predetermined shape was punched from the molded product and used for evaluating each of the physical properties.

[0229]

Comparative Example 10

First, 25 parts by weight of Ubesta 3012U (Ube Industries, Ltd.) was added to 100 parts by weight of MBAM, and the resultant mixture was kneaded for 20 minutes by Labo Plastomill set at 240°C at a rotational speed of 100 rpm to obtain a bulk sample. The resultant sample was heat-pressed at 240°C to obtain a molded product of 2 mm in thickness for evaluating physical properties.

[0230]

A test piece with a predetermined shape was punched from the molded product and used for evaluating each of the physical properties.

[0231]

[Table 3]

Table 3

	Example 12	Comparative Example 10
Polymer	MBAM	MBAM
Thermoplastic resin	3012U	3012U
Compatibilizer	20ANBA7	-
Breaking strength (MPa)	5.29	6.27
Breaking elongation (%)	295.2	226

[0232]

Table 3 (Example 12 and Comparative Example 10) indicates that according to the present invention, the composition containing the acid anhydride group-containing

block copolymer has an improved breaking elongation, and thus desirably acts as the compatibilizer between Ubesta 3012U and MBAM.

[0233]

Example 13

Hydrolytic carboxylation of acid anhydride group-containing acrylic block copolymer and characteristic evaluation

First, 20 g of 20AN3A6 and 40 g of water were placed in a pressure-resistant vessel, and the resultant mixture was heated at 200°C for 2 hours to produce the target carboxyl-containing acrylic block copolymer (referred to as "20C3A6" hereinafter).

[0234]

Conversion of the acid anhydride group to the carboxyl group could be confirmed by IR (infrared absorption spectrum) and ¹³C-NMR analysis (nuclear magnetic resonance spectrum). Namely, in IR analysis, an absorption spectrum at about 1800 cm⁻¹ derived from the acid anhydride group disappeared after conversion.

[0235]

The heat resistance of the resultant carboxyl group-containing acrylic block copolymer was measured by a Kokashiki flow meter. Also, 100 parts by weight of the resultant carboxyl-containing acrylic block copolymer was mixed with 0.2 parts by weight of Irganox 1010 (Ciba

Specialty Chemicals Inc.), and the resultant mixture was melt-kneaded at 50 rpm for 20 minutes with Labo Plastomill (produced by Toyo Seiki Co., Ltd.) set at 240°C to produce a bulk sample. The resulting sample was heat-pressed at 240°C to obtain a molded product of 2 mm in thickness for evaluating physical properties.

[0236]

Example 14

A target carboxyl-containing acrylic block copolymer (referred to as "50C3A6" hereinafter) was produced by the same method as in Example 13 except that 50AN3A6 was used. Also, samples for evaluating physical properties were formed by the same method as in Example 13.

[0237]

Example 15

A target carboxyl-containing acrylic block copolymer (referred to as "100C3A6" hereinafter) was produced by the same method as in Example 13 except that 100AN3A6 was used. Also, samples for evaluating physical properties were formed by the same method as in Example 13.

[0238]

[Table 4]

Table 4

	Example		
	13	14	15
Polymer	20C3A7	50C3A7	100C3A7
Hardness JIS-A	47	51	21
Breaking strength (MPa)	11.7	10.1	4.8
Breaking elongation (%)	332	248	342
Heat resistance (°C)	173.1	192.1	190.1
Oil resistance (wt%)	13.6	18.5	21.7
Compression set (%) 100°C, 22H	49.5	55.6	42.5

[0239]

Table 4 (Examples 13 to 15) indicates that the carboxyl

group-containing block copolymer produced by hydrolytic ring-opening of the acid anhydride group has excellent compression set at high temperatures and improved heat resistance. It is also found that strength required for molding is maintained. In addition, it is found that the cohesive force is improved by introducing a carboxyl group, but such a block copolymer is a material exhibiting excellent compression set and mechanical strength while maintaining low hardness.

[0240]

Example 16

Hydrolytic carboxylation reaction of acid anhydride group-containing block copolymer

First, 100 parts by weight of 20AN3A6 was mixed with 0.2 parts by weight of Irganox 1010 (Ciba Specialty Chemicals Inc.), and the resultant mixture was extruded and kneaded by a visible extruder (30 mm, L/D = 36) (produced by Research Laboratory of Plastics Technology Co., Ltd.) including two thermomixers (30 mm, L/D = 12) (produced by Noritake Co., Limited) provided at the front end at a rotational speed of 25 rpm and 200°C under the condition in which water was supplied at 0.14 kg/hr under pressure, to obtain a target carboxyl-containing block copolymer (20C3A6). Conversion of an acid anhydride group to a carboxyl group could be confirmed by IR (infrared absorption spectrum) and

^{13}C -NMR (nuclear magnetic resonance spectrum). Namely, in IR analysis, an absorption spectrum at about 1800 cm^{-1} derived from the acid anhydride disappeared after conversion. It was thus confirmed that a carboxyl-containing acrylic block copolymer can be produced by ring-opening reaction of an acid anhydride group using any of various processing machines. It is also found that such a copolymer can be produced by an extruder, thereby simplifying the production process.

[0241]

These results indicate that the acrylic block copolymer of the present invention is rich in flexibility and excellent in mechanical strength, moldability, oil resistance, heat resistance, and thermal decomposition resistance, and is further rich in reactivity. It is also found that a novel composition rich in flexibility, oil resistance, and heat resistance can be obtained by combining the acrylic block copolymer of the present invention with the thermoplastic resin and/or the thermoplastic elastomer. It is further found that the acrylic block copolymer of the present invention can be preferably widely used for automobile, electric, and electronic parts because of excellent oil resistance and heat resistance.

[0242]

[Advantages]

The acrylic block copolymer of the present invention is rich in flexibility and excellent in mechanical strength, moldability, oil resistance, heat resistance, and thermal decomposition resistance, and is further rich in reactivity. Therefore, the acrylic block copolymer of the present invention can be preferably used as a novel thermoplastic elastomer, a compatibilizer, and the like. By utilizing these characteristics, the novel acrylic block copolymer of the present invention and a composition containing the block copolymer can be preferably widely used for automobile, electric, and electronic parts.

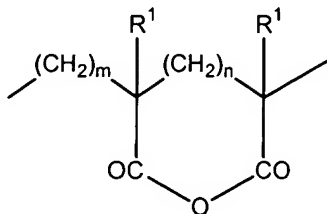
[Name of Document] ABSTRACT

[Abstract]

[Object] To provide a novel acrylic block copolymer rich in flexibility and excellent in mechanical strength, moldability, oil resistance, heat resistance, and thermal decomposition resistance, and further rich in reactivity, and also provide compositions and automobile, electric, and electronic parts, all of which include the acrylic block copolymer.

[Solving Means] The acrylic block copolymer includes a methacrylic polymer block (A) and an acrylic polymer block (B), at least one of the polymer blocks containing, in its main chain, at least one acid anhydride group (C) represented by formula (1):

[Chem. 1]



(wherein R¹s each represent hydrogen or a methyl group and may be the same or different, n represents an integer of 0 to 3, and m represents an integer of 0 or 1).

[Selected Figure] No